

**ATLANTA PM<sub>2.5</sub>, 1999-2008: ASACA DATA TRENDS, QUALITY, AND  
APPLICATION TO ION SENSITIVITY ANALYSIS**

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**ATLANTA PM<sub>2.5</sub>, 1999-2008: ASACA DATA TRENDS, QUALITY, AND  
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## SUMMARY

Beginning in March 1999 at Georgia Institute of Technology, the ASACA (Assessment of Spatial Aerosol Composition in Atlanta) program has provided PM<sub>2.5</sub> concentration and speciation using particle concentration monitoring in and around metropolitan Atlanta. Since 1999, three of the ASACA sites have collected PM<sub>2.5</sub> in an urban setting: Fort McPherson (FT, SW), South Dekalb (SD, SE), and Tucker (TU, NE). In January 2007, TU was retired and Fire Station 8 (FS8, NE) was employed as the new urban site. Starting in 2002, PM<sub>2.5</sub> concentrations have also been characterized at a rural site, Fort Yargo (YG). Water-soluble ionic species and carbonaceous species concentrations are collected daily on filters using a three-channel particulate composition monitor (PCM).

This study summarizes spatial and temporal characteristics of PM<sub>2.5</sub> during the past ten years (1999-2008) of ASACA. Also, ASACA data quality is analyzed using 14 analyses in order to assess the accuracy of the data set and to understand temporal changes in PM<sub>2.5</sub> data quality. The daily data PM data quality is quantified on a scale of 0-10 (0 – worst quality, 10 – best). Various sensitivity analyses were also performed in ISORROPIA, a gas-aerosol phase partitioning model, using the ASACA data set as well as SEARCH data from the Jefferson St. site (JST) to understand the temporal and spatial variation in the limiting components of secondary inorganic aerosol formation in the Atlanta region. ISORROPIA focuses on sulfate, nitrate, and ammonium aerosols. The limiting component is defined as the species that, when perturbed, causes the greatest change in total PM<sub>2.5</sub> mass. From 1999 to 2008, average PM<sub>2.5</sub> concentrations range from

12.9  $\mu\text{g}/\text{m}^3$  at YG to 15.4  $\mu\text{g}/\text{m}^3$  at TU. Sulfate and organic matter are the main components of Atlanta PM, contributing around 26% and 31% respectively to PM mass. A factor of 1.6 is used to convert measured organic carbon concentration to organic matter to account for oxygen, hydrogen and other molecules.

Overall ASACA data quality increased from around 5 in 1999 to a value of 9 in 2005. Seasonal PM data quality appears to be significantly affected by volatility of secondary aerosol species during warm months because ionic data quality regularly decreases in the summer.

The calculated sensitivity of  $\text{PM}_{2.5}$  mass to a perturbation in total (gas + aerosol) nitrate concentration and the relative availability of neutralizing ammonia consistently peak during winter months. PM sensitivities due to changes in total ammonia concentration peak during summer months when sulfate concentrations are high. PM is more sensitive to total sulfate concentration than nitrate and ammonia year-round. Sensitivity to sulfate also shows seasonal variation, although the difference in seasonal maximums and minimums is smaller than that of nitrate and ammonia.

## CHAPTER 1: INTRODUCTION

Numerous studies have linked atmospheric particulate matter (PM) exposure to increased morbidity and mortality (Dockery, Pope et al. 1993; Dockery 2001). PM<sub>2.5</sub> (particulate matter with aerodynamic diameter less than 2.5 µm) can pass into the deep lungs, causing adverse cardio-vascular and cardio respiratory effects (Rosenkranz 1996; Morgan, Reger et al. 1997; Mauderly 2001; Utell, Frampton et al. 2002; Reed, Gigliotti et al. 2004). PM also affects the natural environment by disrupting photosynthesis (Bergin, Greenwald et al. 2001), reducing visibility (Charlson 1969), and degrading materials (Wark, Warner et al. 1998). In July of 1997, the US Environmental Protection Agency (USEPA) issued a National Ambient Air Quality Standard (NAAQS) for PM<sub>2.5</sub> (USEPA 1997) at 35 µg/m<sup>3</sup>. The standard was challenged and removed in 1999, and re-implemented in 2001.

In 1998, the USEPA implemented the Particulate Matter Supersite Program in an effort to characterize PM and support health research (EPA 2000). As a result, researchers have gained an improved understanding of chemical and physical characteristics of aerosols, which help in developing state implementation plans and effective risk management (Sioutas, Pandis et al. 2004; Watson, Chen et al. 2008; Wexler and Johnston 2008).

Particulate matter is either emitted directly into the atmosphere (primary aerosol) or formed in the atmosphere by chemical or physical transformation of precursor gases (secondary). Major sources of primary PM are internal combustion engines, coal-burning power plants and other industrial processes, and even meat-cooking (Habibi 1973;

Lowenthal, Zielinska et al. 1994; Schauer, Rogge et al. 1996; Lim and Turpin 2002).

Diesel engine exhaust is a major contributor to primary PM in cities and has been linked to lung cancer and exacerbation of asthma (Reed, Gigliotti et al. 2004). Secondary aerosols consist mostly of organic matter and inorganic ions such as sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ) and ammonia ( $\text{NH}_4^+$ ).

Partitioning of semi-volatile species between the gas and aerosol phase is governed by complex chemical and thermodynamic principals that need to be understood to help predict affects of changes in primary emissions to aerosol formation (Takahama, Wittig et al. 2004). A number of computational models have been developed that predict this complex behavior and have incorporated into large scale models or used alone to investigate  $\text{PM}_{2.5}$  responses to changes in precursor concentrations (Ansari and Pandis 1998; West, Ansari et al. 1999; Blanchard and Hidy 2003). ISORROPIA is a thermodynamic model that determines equilibrium concentrations of sulfate, nitrate, ammonium and there precursor gases at a specific relative humidity and temperature and elemental composition (Nenes, Pandis et al. 1999). This program is used, along with data from an ongoing  $\text{PM}_{2.5}$  collection study, ASACA (Assessment of Spatial Aerosol Composition in Atlanta), to understand the temporal characteristics of secondary aerosol formation in Atlanta.

Similar to the US Supersite program, ASACA is an effort in to understand speciation, concentration, and spatial and temporal characteristics of  $\text{PM}_{2.5}$ . Beginning in March 1999, the ASACA program has provided  $\text{PM}_{2.5}$  concentration and speciation information from locations in and around metropolitan Atlanta. Three of the ASACA sites are located in urban/suburban settings: Fort McPherson (FT, SW), South Dekalb

(SD, SE), and Tucker (TU, NE). In January 2007, TU was retired and the instruments were moved to Fire Station 8 (FS8, NE). FS8 had the highest annual average  $PM_{2.5}$  levels measured in Atlanta.  $PM_{2.5}$  concentrations are also characterized at a rural site, Fort Yargo (YG) starting in 2002.

To characterize ambient PM composition, water-soluble ionic species and carbonaceous species concentrations are collected daily on filters using a particulate composition monitor (PCM). Ionic material collected on the filters was extracted and analyzed using ion chromatography (IC). Carbonaceous material collected on the filters was analyzed using thermal-optical transmittance (TOT). Continuous  $PM_{2.5}$  mass and elemental carbon (EC) concentrations have also been measured at some of the ASACA sites using a Tapered Element Oscillating Microbalance (TEOM) and an aethalometer respectively.

This study summarizes spatial and temporal characteristics of  $PM_{2.5}$  during the past ten years (1999-2008) of ASACA data. There has been a varying level of data quality throughout the project due to various analytical and operational issues (Cobb 2006); therefore, ASACA data quality is analyzed in order to assess the accuracy of the data set and to understand temporal changes in  $PM_{2.5}$  data quality.

Sensitivity analyses were performed using ISORROPIA applied to the ASACA data set as well as SEARCH data from the Jefferson St. site (JST) to understand the temporal and spatial variation in the limiting components of secondary inorganic aerosol formation in the Atlanta region. This study focuses on sulfate, nitrate, and ammonium aerosols and their associated precursor gases.

## CHAPTER 2: ASACA METHODS

### *2.1 Ambient instruments*

#### *2.1.1 Particle Composition Monitor (PCM)*

Starting in March, 1999, the ASACA project has been an effort to characterize  $PM_{2.5}$  in Atlanta by using filter based particle composition monitors (PCM), aethalometers, and TEOMs. The PCMs are based on a design developed by the ARA (Applied Research Associates) which consists of four separate channels, although ASACA PCMs consist of only three channels collecting 24-hour samples to analyze ions, metals, and elemental and organic carbon (Hartsell and Edgerton 1998). Currently, there are three ASACA PCMs in the metro Atlanta area (Fire Station 8 – FS8; Fort McPherson – FT; South Dekalb – SD), and another PCM is located in rural NE Atlanta at Fort Yargo State Park (YG) (Figure 1). The PCM at FS8 was moved from Tucker – TU in January, 2007. See Butler (2000) thesis for details on the ASACA design.

The three channels of the PCM include a Teflon-coated cyclone with a cut-point at  $10\ \mu m$  (URG, URG-2000-30ENB), a series of denuders which vary depending on the channel, a WINS impactor with a cut-point at  $2.5\ \mu m$  (URG-2000-30WINS), and a filter. The cut-points of the cyclone and impactor are based on a sampling rate of  $16.7\ L\ min^{-1}$  which is controlled by critical orifices. In channels one and two, two annular glass denuders (URG-2000-30X242-3CSS) coated with sodium carbonate and phosphoric acid are used in series to remove acidic gases and alkaline gases. Channel one collects  $PM_{2.5}$  on a nylon filter (Whatman, #7410-004) which is used to analyze water soluble, inorganic ions and the salts of light organic acids including sodium ( $Na^+$ ), ammonium ( $NH_4^+$ ),

potassium ( $K^+$ ), calcium ( $Ca^+$ ), chloride ( $Cl^-$ ), nitrite ( $NO_2^-$ ), nitrate ( $NO_3^-$ ), sulfate ( $SO_4^{2-}$ ), acetate ( $CH_3COO^-$ ), formate ( $HCOO^-$ ), and oxalate ( $C_2O_4^{2-}$ ). Ion concentrations are quantified by ion chromatography (IC, Dionex, CD20 conductivity detector, GP50 gradient pump, EG40 eluent generator using methanesulfonic acid and potassium hydroxide, LC30 chromatography oven, AS40 automated sampler, and IonPac CS12A and AS11-HC analytical columns).  $PM_{2.5}$  in channel two is collected on a Teflon filter (Whatman, #7592-104) for analysis of trace metals. These filters are stored for targeted analyses. Channel three consists of a parallel plate carbon paper denuder to remove organic gases.  $PM_{2.5}$  is collected on quartz filters (Pall #2500QAT-UP), and elemental and organic carbon (EC, OC) is quantified by a thermal-optical transmittance instrument from Sunset Labs. The typical maintenance procedures are summarized in Table 1. For further maintenance details and filter handling procedures refer to Butler (2000).

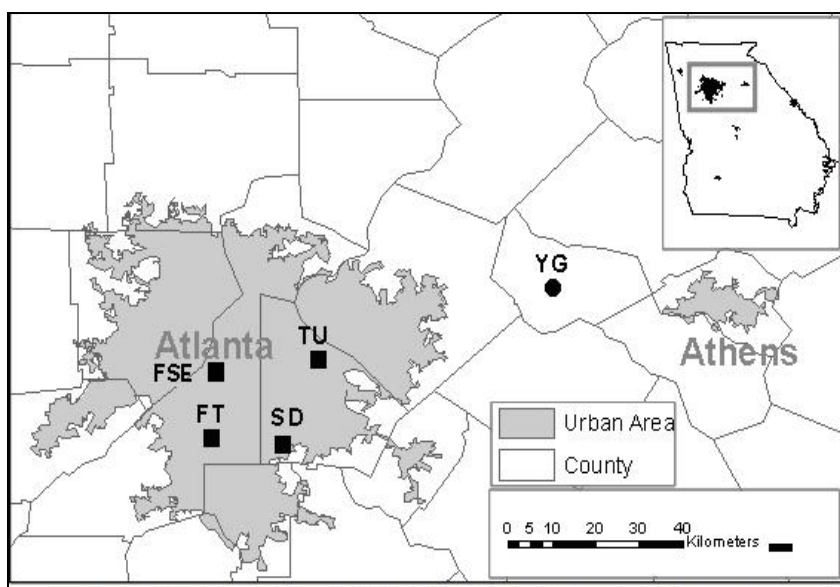


Figure 1- Map of ASACA PM<sub>2.5</sub> monitoring sites (Cobb 2006)

Table 1- PCM schedule of maintenance procedures (Cobb 2006)

PROCEDURE	INTERVAL	DOWNTIME REQUIRED
Cleaning PM <sub>10</sub> Inlet	1 month	10 minutes
Re-coating Annular Denuders	1-2 months	10-20 minutes
Replacing Carbon Denuders	3-6 months	5-10 minutes
Cleaning/Oiling WINS Impactor	1-2 months	10-20 minutes
Flow Calibration	1 week	30-60 minutes
Replacing Solenoid Valves	As needed	30-60 minutes
Replacing Pump	As needed	5-10 minutes

### 2.1.2 Continuous mass monitors

Series 1400a Tapered Element Oscillating Microbalances (TEOM) and aethalometers are used for monitoring continuous total PM<sub>2.5</sub> mass and elemental carbon respectively at the urban ASACA sites. In the TEOMs, after passing through a Teflon-coated 2.5 µm cut cyclone, particles are collected onto a quartz filter which sits on a glass rod oscillating at its natural frequency. The change in the rod's oscillation frequency is detected and is related to the mass collected on the filter. ASACA TEOMs are programmed to collect average mass data at 10-minute intervals. The aethalometers incorporate optical attenuation to quantify EC that collects onto a fibrous filter-tape after passing through a Teflon-coated 2.5 µm cut cyclone at 3 L min<sup>-1</sup>. The amount of light passing through the filter-tape is converted to the EC mass on the filter and is averaged at 5 minute intervals (Hansen 1999.10).



## 2.2 Analytical Procedures

### 2.2.1 Ion Chromatography (IC)

Concentrations of the previously mentioned ionic species are quantified using ion chromatography (IC). After being stored in Petri dishes in a controlled temperature environment, the nylon filters from channel one of the PCMs are placed in vials with 30 mL of 18.1 megaohm, deionized, ultra-pure water. The vials are placed in an iced sonicator bath (Fisher, FS220) for an hour to extract all of the water-soluble ions from the filters. The samples are then refrigerated for at least 24-hours before being analyzed.

Ten standard solutions are used in the IC analysis to create a calibration curve which converts the peak conductivity area of each species to a corresponding concentration. One standard solution is analyzed per five field samples. The conductivity areas are calculated via the Dionex program, PeakNet, and are then converted to liquid concentration. The ambient concentrations of the field samples are calculated using the liquid concentration, flow-rate, and duration of samples via the following equation:

$$Conc_{amb}\left(\frac{\mu g}{m^3}\right) = conc_{liq}\left(\frac{\mu g}{ml}\right) \times \left[ V(ml) / \frac{Q(L/min) \times t(hr) \times 60(min/hr)}{1000(L/m^3)} \right]$$

where,  $V = 30\ ml$

$t = 24\ hr$

$Q = 16.7\ L\ min^{-1}$

### 2.2.2 Thermal-Optical Transmittance (TOT)

Quantification of EC and OC concentrations on the quartz filters from channel three of the PCMs is performed using a thermal-optical transmittance instrument (Sunset Labs Model 3). Field blanks are also analyzed once a month for each site in order to capture the deposition of EC and OC onto the filters from filter pack handling and filter transportation. The average blank concentrations are subtracted from the field sample concentrations. A set of sucrose standards are also analyzed at the beginning and end of the TOT operation in order to ensure the machine's accuracy.

A  $1.47 \text{ cm}^2$  area is cut out of each filter using a punch tool and placed into the TOT sampling oven for analysis. Initially, the temperature in the oven increases to  $870^\circ\text{C}$  during which time the OC is pyrolyzed from the filter in a non-oxidizing carrier gas (He). EC is then removed in the presence of an oxidizing carrier gas (He/O<sub>2</sub>) under a similar temperature profile. The resulting EC and OC concentrations are in terms of carbon mass per filter area (Cary 1998). Ambient concentrations are then calculated from the TOT results by using the flow-rate, duration of sample, and filter area via the following equation:

$$Conc_{amb} \left( \frac{\mu\text{gC}}{\text{m}^3} \right) = conc_{filter} \left( \frac{\mu\text{gC}}{\text{cm}^2} \right) \times \left[ \frac{A(\text{cm}^2)}{\frac{Q(\text{L}/\text{min}) \times t(\text{hr}) \times 60(\text{min}/\text{hr})}{1000(\text{L}/\text{m}^3)}} \right]$$

where,  $t = 24 \text{ hr}$

$$Q = 16.7 \text{ L min}^{-1}$$

$$A = \pi r_{filter}^2 \text{ cm}^2$$

## CHAPTER 3: SPATIAL AND TEMPORAL TRENDS

### *3.1 PM<sub>2.5</sub> Total Mass Trends*

Total PM<sub>2.5</sub> is estimated as the sum of the ambient concentrations of all eleven ions and elemental carbon plus 1.6 times the organic carbon. The factor of 1.6 is used to account for the oxygen and hydrogen that is attached to the OC (Turpin and Lim 2001). Summary statistics of the speciated PM<sub>2.5</sub> collected by the PCM at FT, SD, and TU since March 1999, at FS8 since January 2007, and at YG since February 2002 are shown in Table 2. Average PM<sub>2.5</sub> concentrations range from 12.9 µg/m<sup>3</sup> at YG to 15.4 µg/m<sup>3</sup> at TU. Of the four urban ASACA sites, FS8 has the lowest PM<sub>2.5</sub> average concentration at 13.5 µg/m<sup>3</sup>. However, this is deceptive because the yearly averaged PM<sub>2.5</sub> levels (Figure 2) have been decreasing since 2001 and that, since its inception in 2007, FS8 has experienced significantly higher concentrations of PM<sub>2.5</sub> than the remaining ASACA sites. In 2007 and 2008, FS8 ambient PM<sub>2.5</sub> was 27% greater than that of the other ASACA sites. High concentrations of particulate matter at FS8 are believed to be due to a heavily trafficked industrial road near the station as well as a nearby rail yard. More details on the influences on FS8 are discussed in the subsequent analysis sections of this chapter.

Table 2- Summary of ASACA speciated PM<sub>2.5</sub> (1999-2008)

PM <sub>2.5</sub> (ug/m <sup>3</sup> )	FT (1999-2008)	SD (1999-2008)	TU (1999-2006)	FS8 (2007-2008)	YG (2002-2008)
Average	14.03	14.39	15.36	13.50	12.93
Std Dev	8.39	8.11	8.24	7.52	7.79
Max	57.84	46.96	52.49	62.47	78.18
Min	1.11	1.11	1.12	1.15	1.12
Count	2182	2155	1242	584	646



Figure 2- Annual average speciated PM<sub>2.5</sub> concentrations at all ASACA sites (1999-2008)

ASACA speciated PM<sub>2.5</sub> concentrations exhibit a pattern in seasonal variation (Figure 3). Particulate concentrations peak in the summer for all sites with average levels ranging from 16.4 – 19.9  $\mu\text{g}/\text{m}^3$  at FS8 and TU respectively. Minimum PM concentrations, ranging from 12.9 – 14.6  $\mu\text{g}/\text{m}^3$  at FS8 and SD respectively, occur during the winter months at all sites. PM<sub>2.5</sub> concentrations decrease from summer to winter by 32% at FT, 28% at TU, 22% at SD, 21% at FS8, and 22% at YG. The difference in

seasonal concentration is mostly due to the formation of secondary aerosols by enhanced photochemical activity during the summer. Influences of secondary and primary pollutants on  $PM_{2.5}$  are discussed in further detail in the subsequent sections of this chapter.

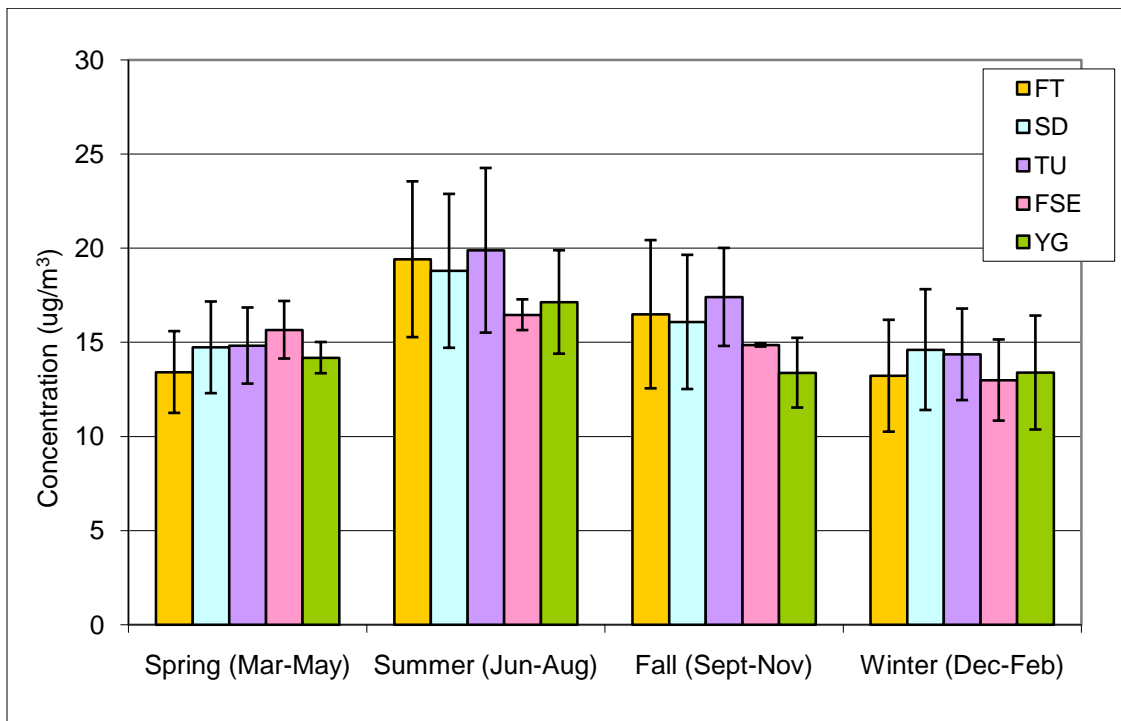


Figure 3- Seasonal averages of the speciated  $PM_{2.5}$  concentrations at all ASACA sites (1999-2008), except for Tucker (1999-2006), Fort Yargo (2002-2008), and Fire Station 8 (2007-2008)

### 3.2 $PM_{2.5}$ Ion Species Trends

Daily averaged ionic species concentrations have been collected via PCM at FT, SD, and TU beginning in March, 1999, at YG since February 2002, and at FS8 since

January 2007. Seven anions and four cations are measured, the most abundant of which are sulfate, nitrate, and ammonium ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ).

Average sulfate concentration ranges from  $3.13 - 4.35 \mu\text{g}/\text{m}^3$  at FS8 and TU respectively (Table 3). Ammonium averages range from  $1.35 - 1.75 \mu\text{g}/\text{m}^3$ , while nitrate ranges from  $0.82 - 1.07 \mu\text{g}/\text{m}^3$ . Sulfate tends to be the greatest ionic contributor to total  $\text{PM}_{2.5}$  mass, regularly making up 24% - 29% (average from 1999-2008 at all ASACA sites) of the mass. Nitrate makes up between 5% - 7% of the  $\text{PM}_{2.5}$  mass, while ammonium makes up 9% - 11%.

Sulfate concentrations tend to peak during the summer months (June – August) and reach a minimum during the winter (December – February) (Figure 4). Summer sulfate peaks decrease from around  $8.5 \mu\text{g}/\text{m}^3$  in 1999 to around  $4.5 \mu\text{g}/\text{m}^3$  in 2003. Sulfate then increases to around  $8 \mu\text{g}/\text{m}^3$  in 2004 and levels off at around  $5.0 \mu\text{g}/\text{m}^3$  from 2006 – 2008. During the summer months in Atlanta, enhanced photochemistry causes oxidation of sulfur dioxide to sulfate. Sulfur dioxide is not oxidized as rapidly during the winter months, with the result that sulfate concentrations rarely exceed  $3 \mu\text{g}/\text{m}^3$ . Seasonal nitrate ambient concentrations peak during the winter at around  $1.4 \mu\text{g}/\text{m}^3$  and have been steadily decreasing since 2002. Average seasonal nitrate reaches a minimum during the summer at around  $0.5 \mu\text{g}/\text{m}^3$ . This observed inverse relationship between nitrate and sulfate is due to the availability of ammonium to neutralize either sulfate or nitrate, as well as higher temperatures, during the summer. High sulfate concentrations take up most of the ammonium, causing nitrate to remain in its gaseous nitric acid form. During the winter, ammonium is available to neutralize nitrate to ammonium nitrate.

Ammonium nitrate is too volatile to exist at higher temperatures, regardless of the availability of ammonium.

Table 3- Major ion statistics at all ASACA sites (1999-2008)

<b>SO<sub>4</sub><sup>2-</sup> (ug/m<sup>3</sup>)</b>	<b>FT (1999-2008)</b>	<b>SD (1999-2008)</b>	<b>TU (1999-2006)</b>	<b>FS8 (2007-2008)</b>	<b>YG (2002-2008)</b>
Average	4.06	3.89	4.35	3.31	3.82
Std Dev	3.15	2.75	3.01	2.42	2.86
Max	31.93	19.46	23.46	16.43	22.62
Min	0.12	0.12	0.13	0.32	0.12
Count	2616	2547	1608	648	615
<b>NH<sub>4</sub><sup>+</sup> (ug/m<sup>3</sup>)</b>	<b>FT</b>	<b>SD</b>	<b>TU</b>	<b>FS8</b>	<b>YG</b>
Average	1.59	1.50	1.75	1.35	1.47
Std Dev	1.07	0.97	1.07	0.80	0.92
Max	9.15	7.24	7.12	5.48	6.90
Min	0.13	0.12	0.15	0.11	0.12
Count	2612	2545	1608	648	618
<b>NO<sub>3</sub><sup>-</sup> (ug/m<sup>3</sup>)</b>	<b>FT</b>	<b>SD</b>	<b>TU</b>	<b>FS8</b>	<b>YG</b>
Average	1.01	0.82	1.07	0.91	0.85
Std Dev	0.80	0.73	0.92	0.66	0.97
Max	7.75	7.53	6.91	3.98	6.84
Min	0.11	0.11	0.11	0.13	0.11
Count	2607	2524	1592	647	625

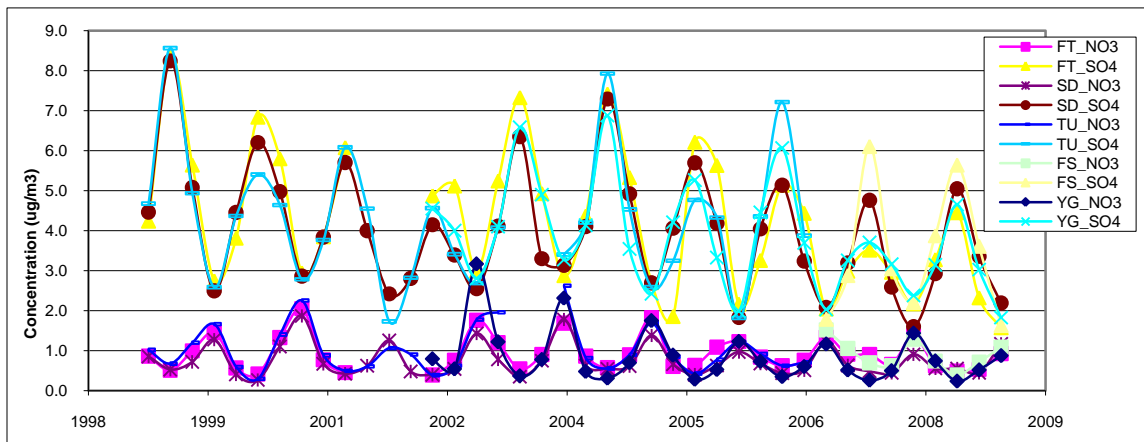


Figure 4- Seasonal average sulfate and nitrate concentrations at all ASACA sites (1999-2008)

Similar to sulfate, ammonium concentrations peak during the summer months and reach a minimum during the winter (Figure 5). Summer ammonium peaks range from  $1.9 - 3.2 \mu\text{g}/\text{m}^3$  while the winter concentrations range from  $0.7 - 1.3 \mu\text{g}/\text{m}^3$ . Summer peaks are caused by ammonia neutralizing the high concentrations of sulfate.

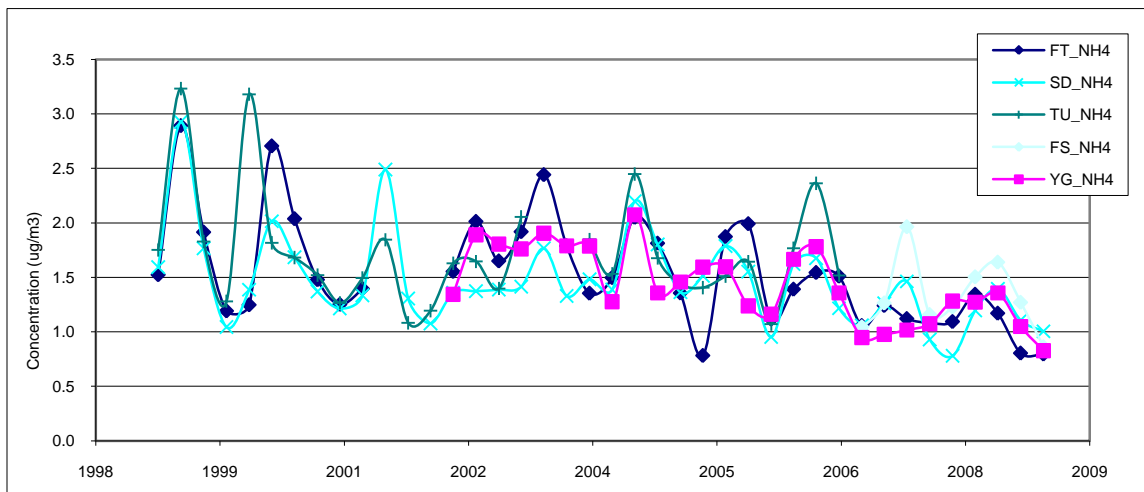


Figure 5- Seasonal average ammonium concentrations at all ASACA sites (1999-2008)

### 3.3 $PM_{2.5}$ Carbonaceous Species Trends

Organic carbon (OC) and elemental carbon (EC) daily averaged concentrations have been collected by a PCM at FT, SD, and TU beginning in March, 1999, at FS8 since January 2007, and at YG since February 2002. TU carbon data collection stopped in 2006. A summary of the ASACA OC and EC statistics as well as the ratio of OC to EC



from 1999 – 2008 are shown in Table 4. OC/EC ratios are generally unique to a specific site and are commonly used to describe the pollution influences at a site.

Average OC ambient concentrations range from  $4.49 - 4.89 \mu\text{g}/\text{m}^3$ . OC contributes around 30% - 33% to  $\text{PM}_{2.5}$  mass. OC is often multiplied by a factor in order to account for the oxygen and hydrogen that is typically associated with OC. The adjusted value is referred to as organic matter (OM). For the ASACA data, a factor of 1.6 is used (Lim and Turpin 2002). In this case, OM contributes between 48% and 52% to  $\text{PM}_{2.5}$  mass. EC concentrations range from  $0.77 - 1.25 \mu\text{g}/\text{m}^3$  which corresponds to 3.7% - 9.2% of the  $\text{PM}_{2.5}$  mass. OC/EC ratios range from 4.29 at FS8 to 11.59 at YG. Studies suggest that the low OC/EC ratio at FS8 is primarily caused by the influence of diesel engine emissions near the site. There is a rail yard and a highly trafficked industrial road near FS8. YG on the other hand is a rural site and is less influenced by primary traffic pollutants. The high density of vegetation around YG also increases the OC/EC ratio. FT, SD, and TU are all impacted by vehicle emissions but not so much diesel as FS8, as indicated by the relatively low OC/EC ratio at FS8.

OC concentrations tend to peak during the summer and reach a minimum during the winter (Figure 6 and 7). The summer peaks are largely due to increased emissions from vegetation and secondary carbon produced by photochemical reactions. The difference between the summer and winter averages is much less than that of sulfate, indicating that OC is emitted by automobile combustion as well as biomass burning during the winter. The peak OC concentrations have decreased from around  $9.0 \mu\text{g}/\text{m}^3$  in the summer of 2001 to around  $4.9 \mu\text{g}/\text{m}^3$  in 2008. Winter time OC concentrations are typically between  $2.7$  and  $4.5 \mu\text{g}/\text{m}^3$ .

Table 4- The ASACA elemental and organic carbon statistics. Ratio of organic carbon to elemental carbon (1999-2008)

<b>OC (ug/m<sup>3</sup>)</b>	<b>FT (1999-2008)</b>	<b>SD (1999-2008)</b>	<b>TU (1999-2006)</b>	<b>FS8 (2007-2008)</b>	<b>YG (2002-2008)</b>
Average	4.54	4.80	4.89	4.57	4.49
Std Dev	2.76	2.97	2.82	2.69	2.80
Max	38.84	22.36	26.31	29.21	26.84
Min	0.12	0.15	0.11	0.14	0.16
Count	2591	2713	1774	683	655
<b>EC (ug/m<sup>3</sup>)</b>	<b>FT</b>	<b>SD</b>	<b>TU</b>	<b>FS8</b>	<b>YG</b>
Average	0.86	1.10	0.77	1.25	0.49
Std Dev	0.66	0.89	0.56	0.79	0.32
Max	11.85	15.27	3.88	4.94	2.98
Min	0.11	0.11	0.11	0.13	0.11
Count	2599	2709	1756	683	655
<b>OC/EC</b>	<b>FT</b>	<b>SD</b>	<b>TU</b>	<b>FS8</b>	<b>YG</b>
Average	7.14	6.42	9.38	4.29	11.59
Std Dev	5.11	5.45	7.70	2.15	9.89
Max	45.82	51.99	83.02	15.43	157.21
Min	0.13	0.06	0.10	0.26	0.23
Count	2589	2707	1744	683	655

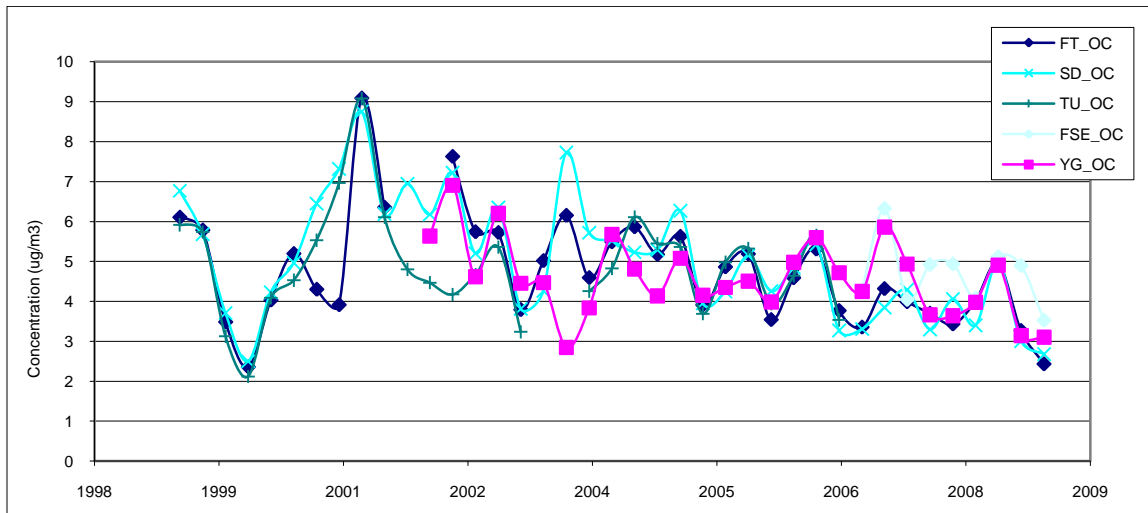


Figure 6- Seasonal average of ASACA organic carbon PM<sub>2.5</sub> (1999-2008)

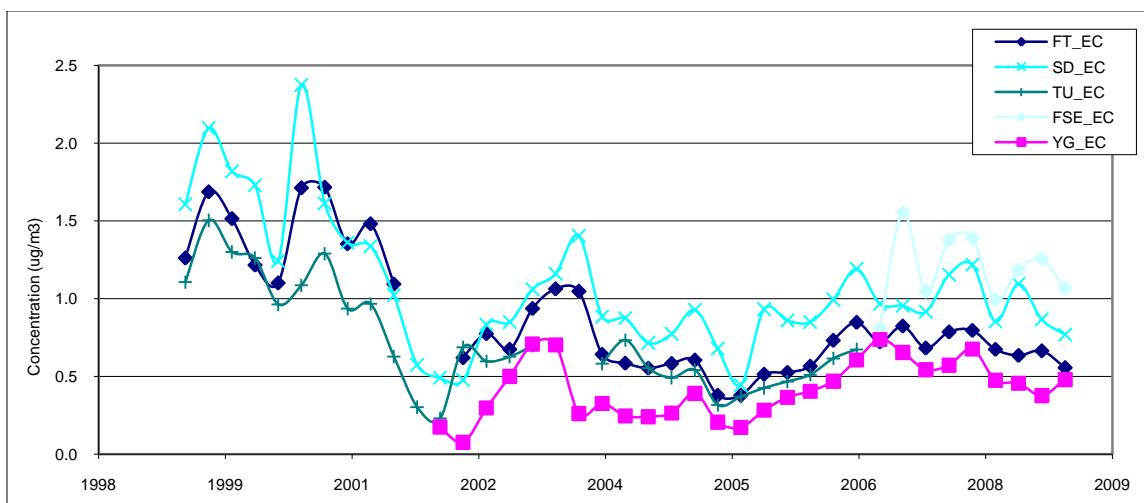


Figure 7- Seasonal average of ASACA elemental carbon PM<sub>2.5</sub> (1999-2008)

Seasonal trends in ambient EC concentrations are less evident since EC is not affected by photochemistry and its sources remain fairly constant throughout the year. YG consistently experiences the lowest concentrations of EC ranging from 0.07 – 0.7  $\mu\text{g}/\text{m}^3$ . The highest concentrations of EC from 1999 to 2007 were at SD, ranging from 0.4 – 2.4  $\mu\text{g}/\text{m}^3$ . Since 2007, FS8 has the highest measured EC ranging from 1.0 – 1.6  $\mu\text{g}/\text{m}^3$ .

The average seasonal OC/EC ratios for all ASACA sites from 1999-2008 are shown in Figure 8. The OC/EC ratio at YG is consistently the highest at around 9.8 to 14.5, while FS8 experiences the lowest ratio at around 4.1 to 4.5. The greatest seasonal variations in OC/EC ratios are observed at YG and FT, having a decrease from summer to winter of 32% and 21% respectively. Seasonal fluctuations in the OC/EC ratio indicate that OC concentrations at YG and FT are probably the most influenced by photochemical reactions. The ratios at TU, SD and FS8 are fairly constant throughout the year at about 9.4, 6.4 and 4.5 respectively. Of these three sites, TU experiences the highest OC/EC ratio possibly because that site is impacted by fresh OC emitted from

combustion in automobiles that are not diesel since it is located in a commercial area and experiences lower densities of industrial related traffic. FS8 ambient  $PM_{2.5}$  however, is impacted by high EC emissions from diesel engines.

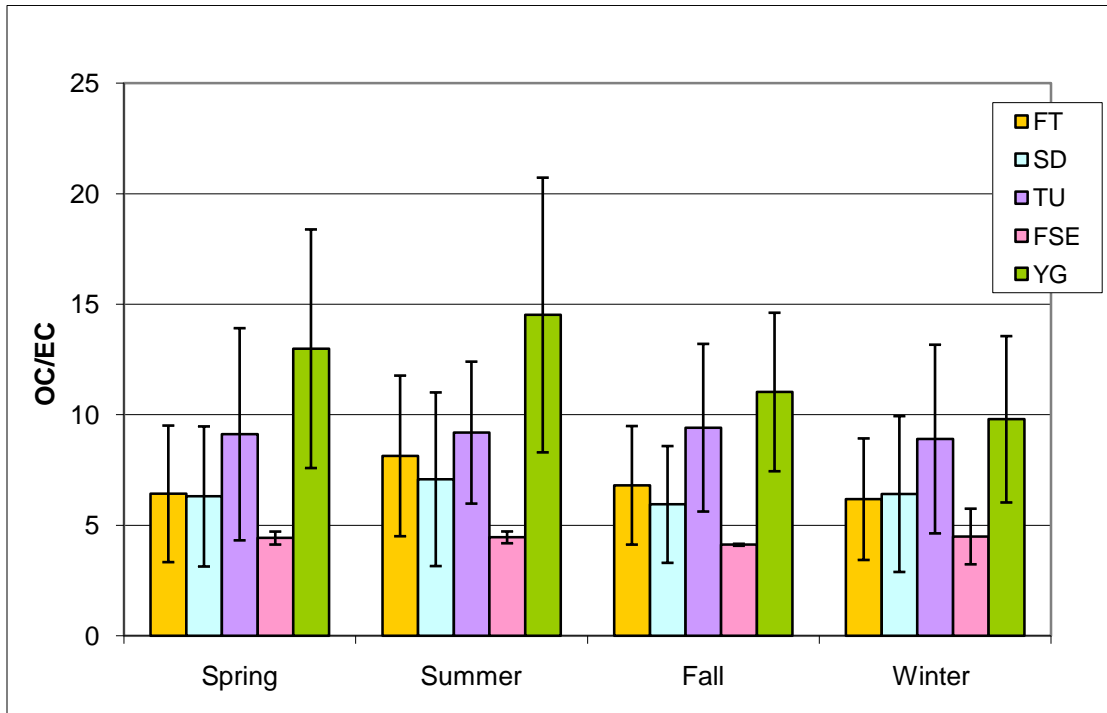


Figure 8- Seasonal average of ASACA OC/EC ratios (1999-2008)

## CHAPTER 4: DATA QUALITY

### *4.1 Analysis Metrics*

Although data capturing and quality assurance procedures are strictly followed, errors occur due to the complexity and number of steps it takes to produce speciated  $PM_{2.5}$  data, as well as less controllable events such as pump malfunction. To ensure data quality and to monitor the state of the ASACA project, the ASACA daily  $PM_{2.5}$  data quality is quantified using 14 analytical metrics. Each day is assigned a data quality value on a scale of 0-10 according to the results of each analysis (0 is the lowest and 10 is the highest). The total  $PM_{2.5}$  data quality is the average of all 14 analysis results. The data are then labeled if part of the speciated  $PM_{2.5}$  appears invalid (1-poor carbon data quality, 2-poor ion data quality, 3-poor aethalometer data quality, 4-poor TEOM data quality). Also, missing data are reported for each day.

Data quality is quantified by comparing components of the  $PM_{2.5}$  data observed at each of the ASACA sites as well as sites operated by other organizations.  $PM_{2.5}$  data from three non-ASACA sites located in Atlanta are used for these analyses. The East River and South Dekalb sites are from Air Quality System (AQS) database which is operated by the Environmental Protection Agency (EPA). The Confederate Avenue site is GA-AMP. The 14 metrics used to analyze data quality and a brief description of each are as follows:

1. Data Comment- comments left by the filter collector/analyzer are tabulated and quantified

2. Ion Equivalence- the anion-to-cation equivalence ratio is calculated and compared to the theoretical value
3. Sulfate site comparison- a comparison of the sulfate mass concentration observed at each of the four ASACA sites
4. OC site comparison- a comparison of the OC mass concentration observed at each ASACA site
5. Mass Closure- speciated  $PM_{2.5}$  mass concentration observed by the PCM compared to the TEOM measurement
6. TEOM site comparison- a comparison of the ASACA TEOM measurements
7. BC/EC comparison- Aethalometer measured BC compared with the TOT measured EC
8. Aethalometer comparison- a comparison of the ASACA Aethalometer measurements
9. East River vs. ASACA PCM- the ASACA sites observed PCM  $PM_{2.5}$  mass concentration compared to the AQS East River site  $PM_{2.5}$
10. East River vs. ASACA TEOM- the ASACA sites observed TEOM  $PM_{2.5}$  mass concentration compared to the AQS East River site  $PM_{2.5}$
11. Confederate Ave. vs. ASACA PCM- the ASACA sites observed PCM  $PM_{2.5}$  mass concentration compared to the GA-AMP Confederate Ave. site  $PM_{2.5}$
12. Confederate Ave. vs. ASACA TEOM- the ASACA sites observed TEOM  $PM_{2.5}$  mass concentration compared to the GA-AMP Confederate Ave. site  $PM_{2.5}$
13. South Dekalb vs. ASACA PCM- the ASACA sites observed PCM  $PM_{2.5}$  mass concentration compared to the AQS South Dekalb site  $PM_{2.5}$

14. South Dekalb vs. ASACA TEOM- the ASACA sites observed TEOM PM<sub>2.5</sub> mass concentration compared to the AQS South Dekalb site PM<sub>2.5</sub>

#### 4.1.1 Data Comment

During filter collection or analysis any irregularity or procedural errors are recorded in field and laboratory notebooks. A data quality value is assigned to the reoccurring comments, some of which are shown in Table 5.

Table 5- Data comments and their associated quality

Comment	DQ value
<24 hrs	2
smoke event	10
12 hrs	5

#### 4.1.2 Ion Equivalence

A charge balance is used to quantify ionic species data quality. The anionic and cationic equivalencies are calculated using ambient concentrations by the following equations:

$$Cation_{-eq} \left( \frac{\mu eq}{m^3} \right) = \left( \frac{[Na^+]}{22.989} \right) + \left( \frac{[NH_4^+]}{18.04} \right) + \left( \frac{[K^+]}{39.098} \right) + \left( \frac{2*[Ca^{2+}]}{40.078} \right)$$

$$Anion_{-eq} \left( \frac{\mu eq}{m^3} \right) = \left( \frac{[Cl^-]}{35.453} \right) + \left( \frac{[NO_3^-]}{62.005} \right) + \left( \frac{2*[SO_4^{2-}]}{96.062} \right) + \left( \frac{[NO_2^-]}{46.006} \right) + \left( \frac{[CH_3COO^-]}{59.049} \right) + \left( \frac{[HCOO^-]}{45.016} \right) + \left( \frac{2*[C_2O_4^{2-}]}{88.016} \right)$$

The ion equivalence data qualities are determined by the anion to cation equivalence ratio according to the values in

Table 6. The data receive a score of 10 if the equivalence ratio is within a 25% deviation from 1. The quality decreases as the equivalence varies further from 1 at 25% increments. Figure 9 illustrates a period at Fort McPherson (Jan 06 – Mar 07) in which data points fall into the various data quality “bins”. The graph indicates that most of the data points are assigned a quality value of 8. Outlying data are primarily due to IC analysis error, filter preparation and handling errors or filter condition. Poor ion equivalence data quality is often attributed to moisture collected on the filter during rainy periods due to a small leak in the filter pack assembly.

Table 6- Quality value regimes used for ion equivalence ratios

<b>Quality</b>	<b>Anion/Cation ratio</b>	
	<b>min</b>	<b>max</b>
10	0.9	1.3
8	0.667	1.5
6	0.5	2
4	0.4	2.5
2	0.333	3
0	0	infinity



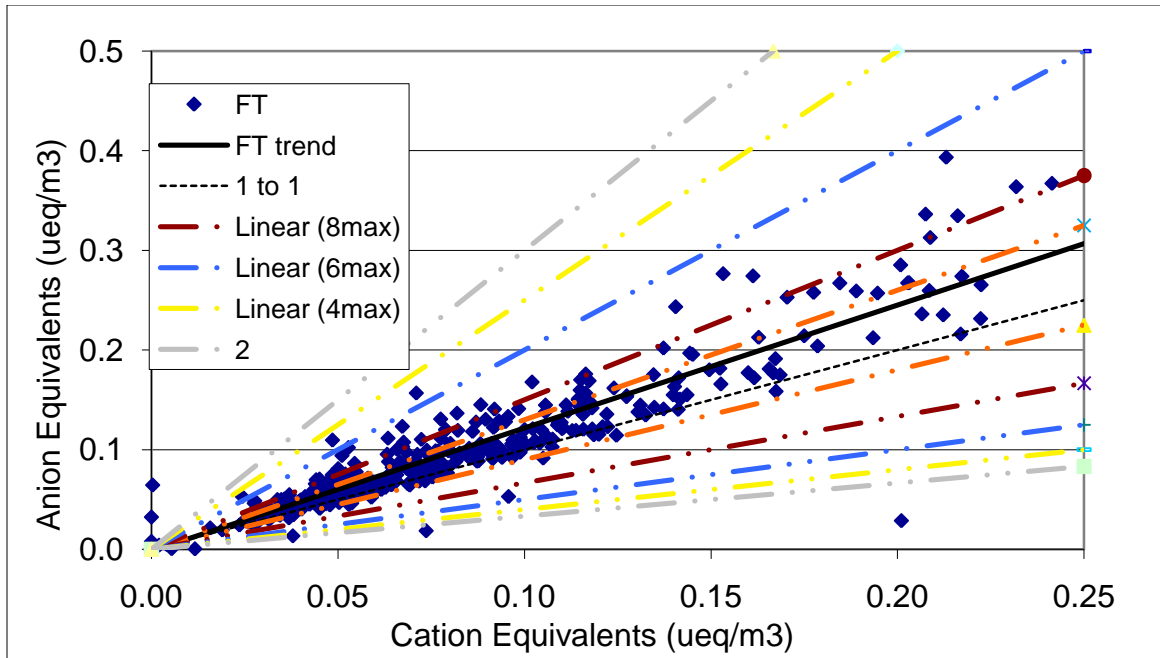


Figure 9- Anion vs. cation charge equivalence at FT and the data quality value bins (Jan 06-May 07)

The yearly averaged ion equivalence data quality for each ASACA site is shown in Figure 10. The lowest data quality occurred in the year 2002 at all the sites with values ranging from 4.2 at YG to 5.1 at FT. Ion data quality reached its peak in 2004 and maintained until 2006 at around 9. Data quality increases from 2007 to 2008, and data from the first six months of 2009 suggest an even greater increase.

Because the ion equivalence metric captures laboratory procedural quality rather than field procedure quality, all of the sites tend to have similar annual mean data qualities. A decrease in the YG data quality during 2004 is an exception. This is most likely due to the lack of data sampling during that time period since missing data is given 0 quality points. Similarly, the decrease in data quality from 2000 to 2002 can be partially attributed to a lack of data. However, the increase from 2002 to 2003 indicates

the presence of other problems since number of data available is nearly the same for both years at all sites. There are also periods from 2000 to 2002 in which some of the ionic species are missing from the data. For example, if all of the cation mass concentrations seem too low or are missing for a month, there was an issue while running the samples in the IC.

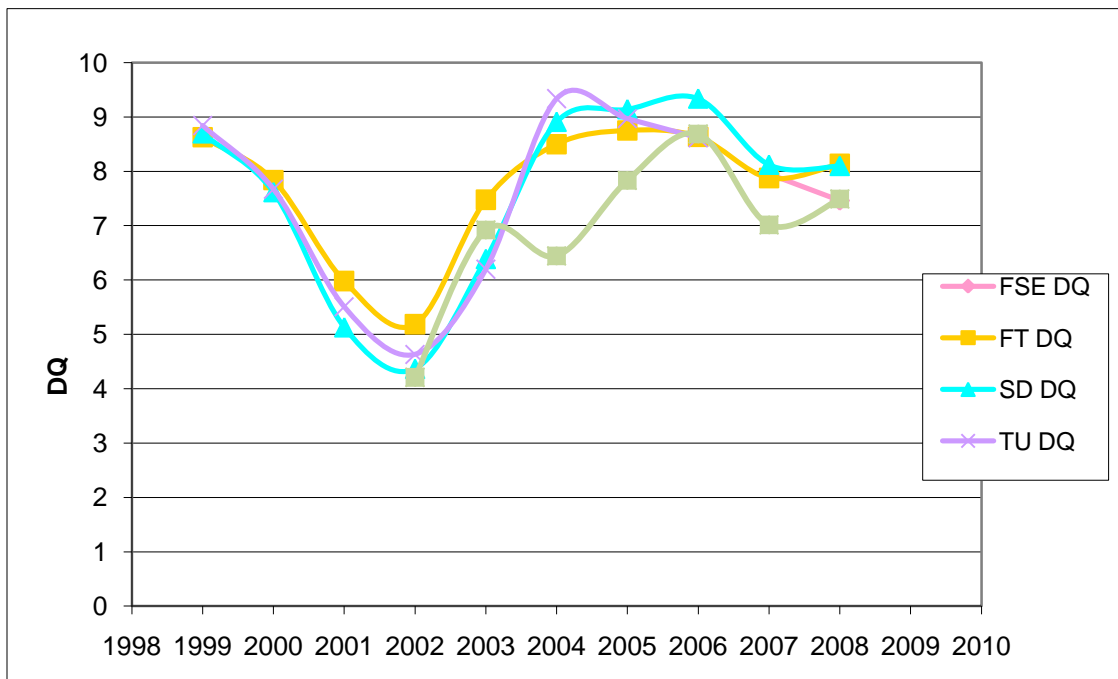


Figure 10- Average annual ion equivalence data quality (99-08)

#### 4.1.3 Sulfate Site Comparison

A comparison of the daily ambient sulfate mass concentration is performed to better capture the data quality of the ionic constituents of  $PM_{2.5}$ . Unlike the ion equivalence metric, the sulfate site comparison metric describes site specific quality issues. Sulfate is used in this comparison because, being a secondary pollutant, its concentrations tend to be relatively ubiquitous on a local setting.

Ambient sulfate mass concentrations recorded at the urban ASACA sites (FS8, FT, SD, TU) are used for the initial analysis equations shown below. The coefficient of divergence (COD) is calculated for each site pair and compared to the daily mass difference value for the same site pair as shown in the equations below. For any day there will only be three site pairs since FS8 and TU data do not overlap temporally. A data quality value is assigned to the site pair depending on their correlation. The site specific data quality value is then taken to be the maximum of the site pair data quality values. For a visual reference to this analytical process see Figure 11 which follows a particular day in the sulfate site pair comparison during 2007-2008. This is a less strict method than the ion equivalence metric because more variance is expected at the different sites.

$$COD_{ij} = \sqrt{\frac{1}{n} \sum_{alldays} \left( \frac{x_i - x_j}{x_i + x_j} \right)^2} ; \text{sites } i, j, k \text{ (FSE/TU, FT, SD)}$$

$$\begin{aligned} \text{if diff} = \frac{x_i - x_j}{x_i + x_j} < COD_{ij} & ; DQV_{ij} = 10 \\ & < 2 * COD_{ij} ; DQV_{ij} = 5 \\ & > 2 * COD_{ij} ; DQV_{ij} = 0 \end{aligned}$$

$$DQ_i = \max(DQV_{ij}, DQV_{ik})$$

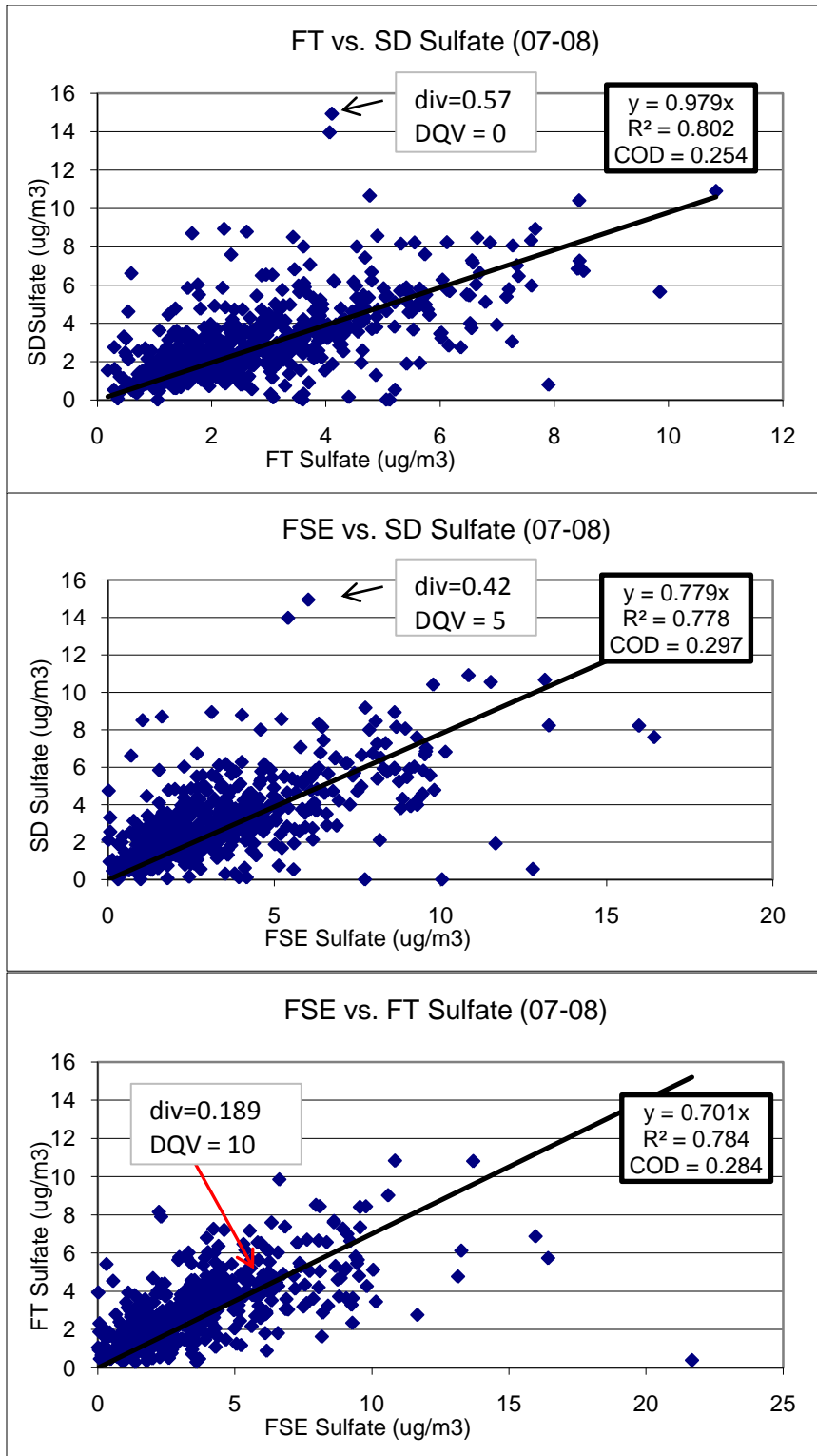


Figure 11- Sulfate site comparisons and data quality calculation for one day:  $DQ_{FS8} = \max(DQV_{FS8/FT}, DQV_{FS8/SD}) = 10$ ,  $DQ_{FT} = \max(DQV_{FS8/FT}, DQV_{FT/SD}) = 10$ ,  $DQ_{SD} = \max(DQV_{SD/FT}, DQV_{FS8/SD}) = 5$

Yearly averages of the sulfate data quality are shown in Figure 12. A minimum data quality of 1.2 is seen at TU in 2003. FT and YG have minimum values in 2002 of 2.5 and 5.6 respectively, while SD reaches its minimum in 2000. Data quality tends to increase for all sites from 2003 to 2004 to a maximum value of 9.3 at SD. While TU experiences a sharp drop in data quality just before it is retired, quality at the remaining sites is maintained between 7 and 9 with the exception of YG in 2007. The poor data quality observed from 2000 to 2003 is most likely explained by a lack of samples due to poor site maintenance.



Figure 12- Average annual sulfate site comparison data quality (99-09)

There are a few situations that this metric does not accurately describe the ionic data quality. One issue occurs when two of the three urban sites experience poor data quality while the third does not since only three sites are used in the initial comparison of

this quality analysis method. The result is that the site with good actual data quality would appear in the analysis to have poor data quality when compared to the other two sites. Also, interesting data points caused by events taking place at one site rather than all three could be given a low data quality score. A controlled burn plume passing through one site is an example of an interesting data point. Another issue is that this metric does not account for errors related to the ASACA system as a whole. The implementation of non-ASACA site comparison metrics is an attempt to solve these problems.

#### *4.1.4 Organic Carbon Site Comparison*

The data quality of the daily OC concentrations at each ASACA site is calculated via the same process as the sulfate site comparison. A data quality value is assigned to each OC/EC measurement by comparing the site pair difference coefficient to the coefficient of divergence for the same site pair. The OC site comparison metric is affected by both the field procedures and the laboratory analysis of the filter.

The yearly averaged OC data quality at each ASACA site is shown in Figure 13. Similarly to the sulfate site comparison results, a minimum value is observed at TU in 2003 and quality peaks at 9.22 in 2004 at FT. SD and YG also experience minimum values in 2003 while FT has a minimum in 2002. With a few exceptions, the overall OC data quality trend follows a similar pattern as the sulfate data quality. The close correlation of these metrics suggests there are some major issues affecting the data quality of both the ion and carbon PM<sub>2.5</sub> species. Site maintenance and missing data may be an issue that affects both of these species. Periods during which the sulfate and OC

data quality do not correlate indicate PCM channel specific quality issues rather than site specific issues. For example, separate pumps are used for all three channels and, although flowrates are checked weekly, one channel may experience a change in flow while the others do not.



Figure 13- Averaged annual OC site comparison data quality (99-09)

The OC site comparison's ability to describe carbon aerosol data quality is limited by the same issues as the sulfate site comparison. Interesting data points may be marked as unreliable and ASACA system inaccuracies are not captured.

#### 4.1.5 Continuous Measurement Data Quality

Continuously measured data include total  $PM_{2.5}$  measured by a TEOM and BC measured with an aethalometer. The 24 hour averages of each data set are analyzed for

quality assurance via the same process as the sulfate site comparison metric. A mass closure analysis is performed by comparing total TEOM PM<sub>2.5</sub> ambient concentration to the speciated PM<sub>2.5</sub> concentration from the PCM. TEOM PM<sub>2.5</sub> concentrations at each site are compared to each other in a similar way. The aethalometer BC is compared to the EC recorded at the same site by the TOT. Aethalometer BC is also compared from site to site within the ASACA network.

Figure 14 and 15 show the yearly mass closure and TEOM comparison results for the periods that TEOM data are available. Mass closure analysis is only performed on days in which all of the components of PM<sub>2.5</sub> data are available so that missing data does not impact the mass closure data quality results. Mass closure data quality has remained between 7 and 10 at all of the sites from 1999 to 2008. TU regularly experiences the lowest data quality, while the rest of the sites rarely dip below 8. On the other hand, the TEOM comparison metric indicates a rise in data quality from 1999 to 2005 and an overall decrease from 2006 to 2008. FS8 and FT reach a minimum value of 5.2 and 4.6 respectively in 2008. While differences in actual PM<sub>2.5</sub> concentrations at each site may explain some of the poor TEOM comparison quality, the major decrease after 2005 is caused by the sporadic sampling periods of the TEOM. In 2005 each TEOM collected over 300 days worth of PM data, while in 2007 and 2008 the number of days recorded at FS8 decreased to 150 and 88 respectively.



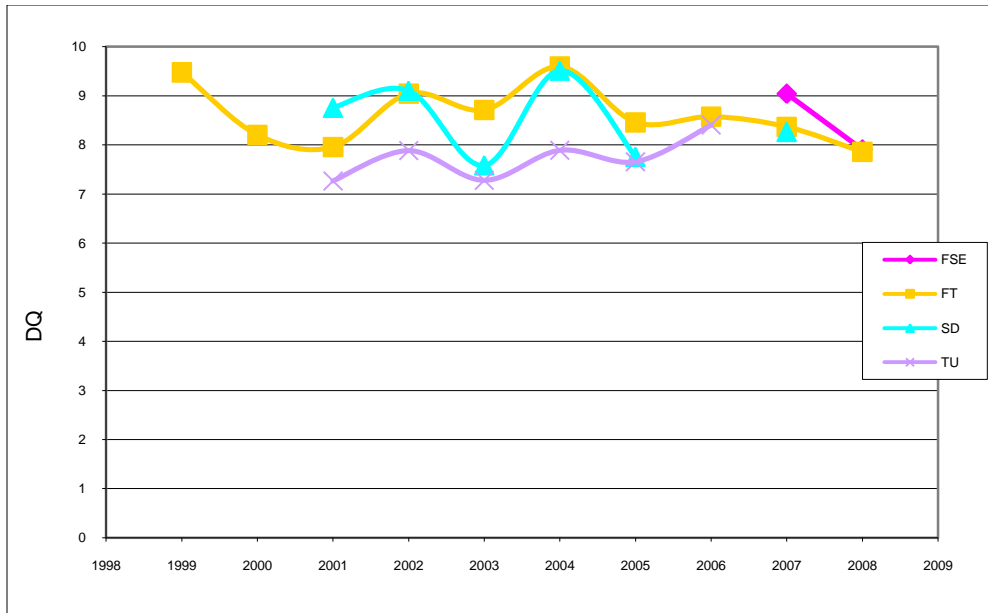


Figure 14- Average annual mass closure data quality (1999-2008)

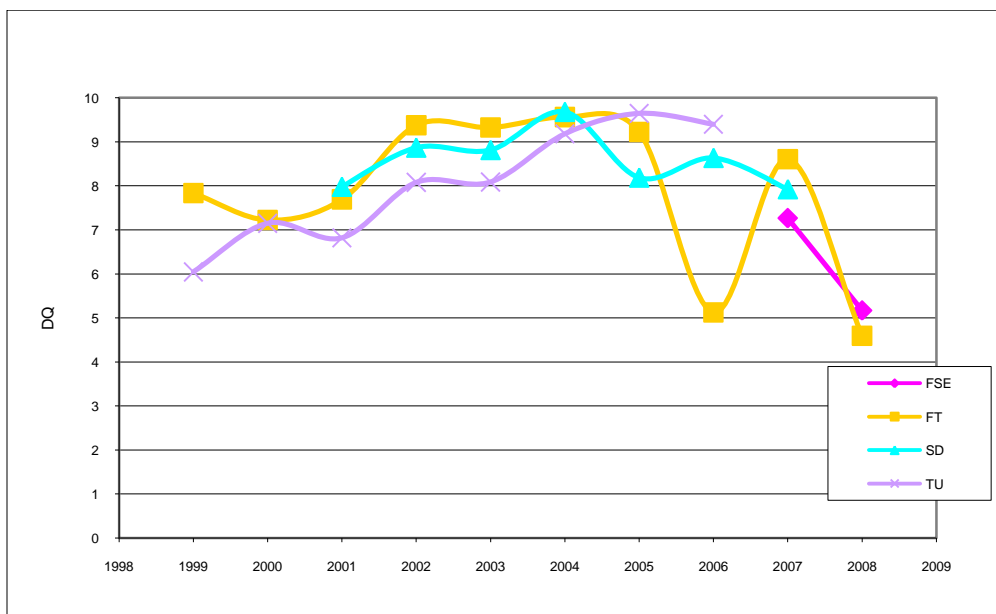


Figure 15- Average annual TEOM site comparison data quality (99-08)

The results of the Aethalometer BC vs. TOT EC and Aethalometer site comparison metrics are shown in Table 7 and 8. Data quality values range from 6 to 9 at FS8, SD and FT for both comparisons. The BC vs. EC quality is not expected to be 10 because of the BC and EC are measured differently and therefore represent qualities of PM. Also the Aethalometer comp quality is not expected to be too high because EC is a primary pollutant and is less ubiquitous on a local setting than sulfate of OC.

Table 7- Average annual TOT EC vs. Aethalometer BC data quality

<b>TOT vs. Aeth</b>	<b>FS8</b>	<b>FT</b>	<b>SD</b>
<b>2007</b>	8.25	7.84	6.57
<b>2008</b>	6.75	6.68	7.61

Table 8- Average annual aethelomter site comparison data quality

<b>Aeth site comp</b>	<b>FS8</b>	<b>FT</b>	<b>SD</b>
<b>2007</b>	8.02	6.61	6.53
<b>2008</b>	8.98	6.57	8.78

#### *4.1.6 Non-ASACA Site Comparison*

Total 24 hour PM<sub>2.5</sub> data collected at three sites that are not part of the ASACA project are compared to the daily ASACA speciated PM<sub>2.5</sub> and TEOM data for further data quality analysis. Because missing data is accounted for by previously mentioned metrics, this analysis is only performed on days in which all of the components of ASACA PM<sub>2.5</sub> data are available. This way, any missing data components do not have an impact on the averaged data quality results. The yearly averaged data quality results

from the East River and South Dekalb comparisons are shown in Figure . A summary of the Confederate Avenue comparison is located in Table 5.

According to these metrics, the PCM speciated  $PM_{2.5}$  from all ASACA sites experiences a dip in data quality from 2002 to 2003 when compared to East River and South Dekalb sites. This reinforces the proposed theory that poor data quality observed in 2002 by previously mentioned metrics is primarily due to missing data, while system errors have a greater influence on 2003 data quality. Furthermore, the TEOM site comparison data quality from the non-ASACA site comparison maintains a value of around 9 at all sites, indicating that the errors mainly occurred within the ASACA data collection network rather than at the non-ASACA sites.

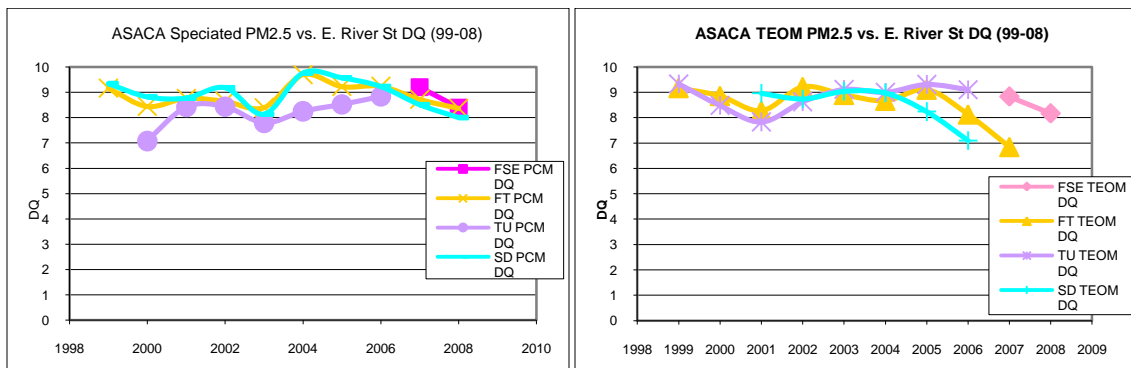


Figure 16- Average annual non-ASACA site comparison data quality (99-08)

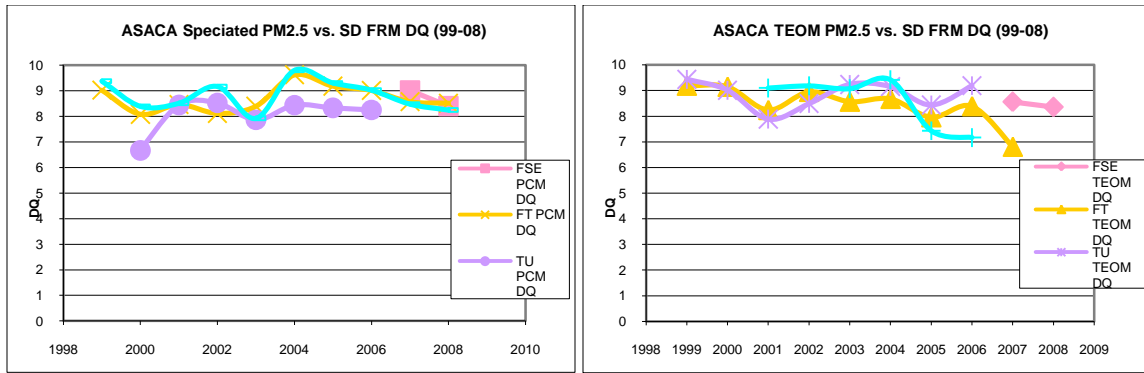


Figure 16- (continued)

Table 9- Average annual Confederate Avenue site comparison data quality

Confederate Ave.	FS8 TEOM	FS8 PCM	FT TEOM	FT PCM	TU TEOM	TU PCM	SD TEOM	SD PCM
2005	--	--	9.31	9.79	8.11	8.41	8.62	8.56
2006	--	--	8.95	8.82	8.78	8.26	8.23	8.87
2007	9.03	9.08	7.81	8.38	--	--	--	8.58
2008	8.46	8.51	--	7.89	--	--	--	8.42

#### 4.1.7 $PM_{2.5}$ Quality Summary

The results from each of the 14 metrics is averaged and recorded as the  $PM_{2.5}$  total data quality. The yearly averaged  $PM_{2.5}$  data quality from each ASACA site is shown in Figure 17. The minimum data quality occurs at the inception of the ASACA project in 1999 and steadily increases until 2004. The data quality decreases at FT and SD from 2005 to 2008 from 8.5 to 6.6 and 6.5 respectively. The data quality for the incomplete 2009 data set suggests that data quality will increase for that year.

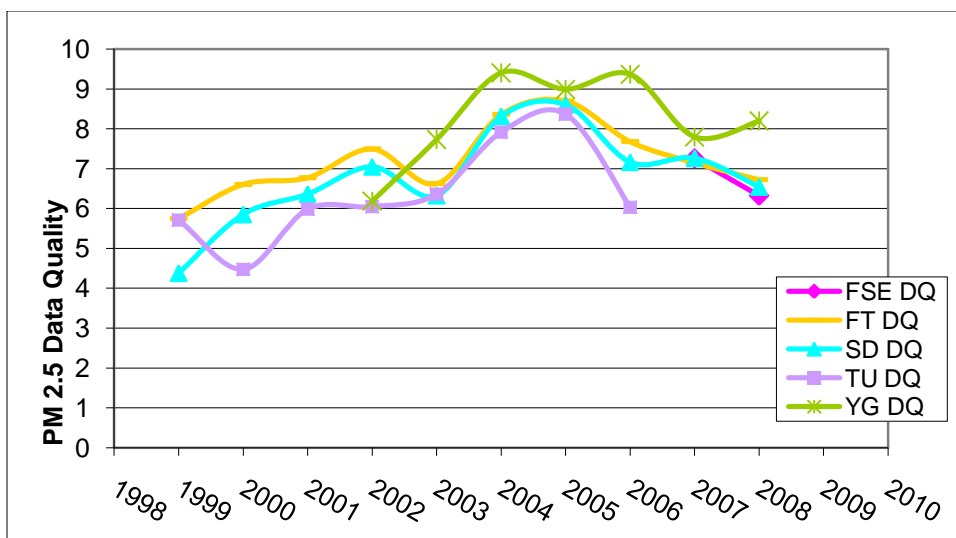


Figure 17- Average annual total PM2.5 data quality

The data quality was also averaged for each season and is shown in Figure 18. Seasonal data quality is highest for all ASACA sites during the winter and spring months (December – February and March – May respectively). The seasonal minimum occurs during the summer months at all of the sites. YG and TU experience a 10% and 20% decrease in data quality respectively from spring to summer. To further investigate possible factors influencing the seasonal variation in PM<sub>2.5</sub> data quality the seasonal averages of the percentage of poor ion data quality days and poor carbon quality days shown in Figure 19. The seasonal maximum and minimum poor carbon data quality days occur during the spring and winter months respectively at TU, FT, and SD while the max and min occur during the summer and winter at FS8 and YG. A more defined seasonal trend is observed for the seasonal poor ion data quality days. All sites experience a maximum poor ion quality days during the summer months. Increased volatility of certain secondary species could be an explanation the poor data quality days during the summer. Seasonal variations of carbon data quality at YG are more similar to the

seasonal ion data quality trends than at the urban sites, further emphasizing the impact of secondary aerosol volatility on data quality since YG carbonaceous aerosol has a higher fraction of secondary carbon than at the urban sites.

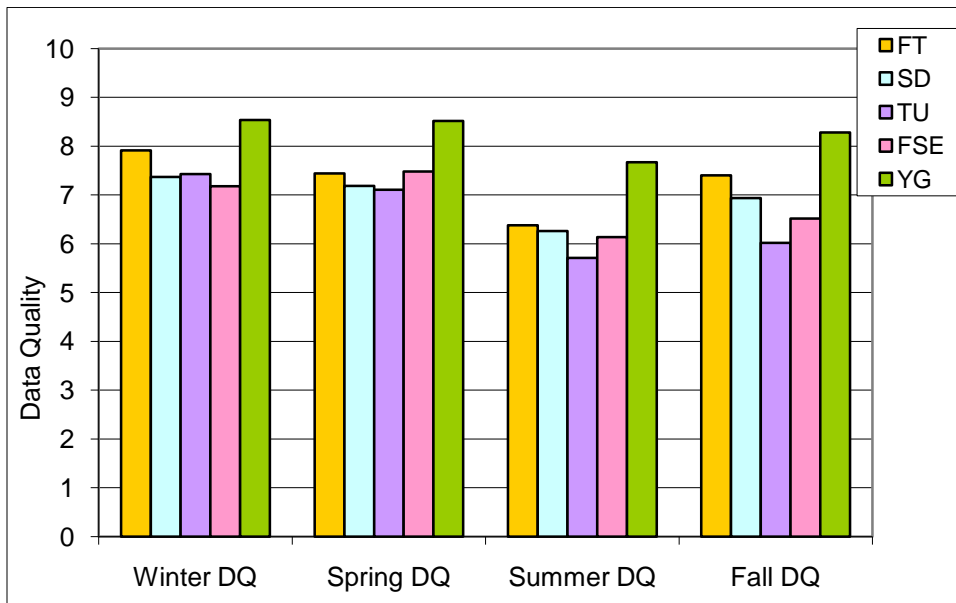


Figure 18- Average seasonal PM2.5 data quality

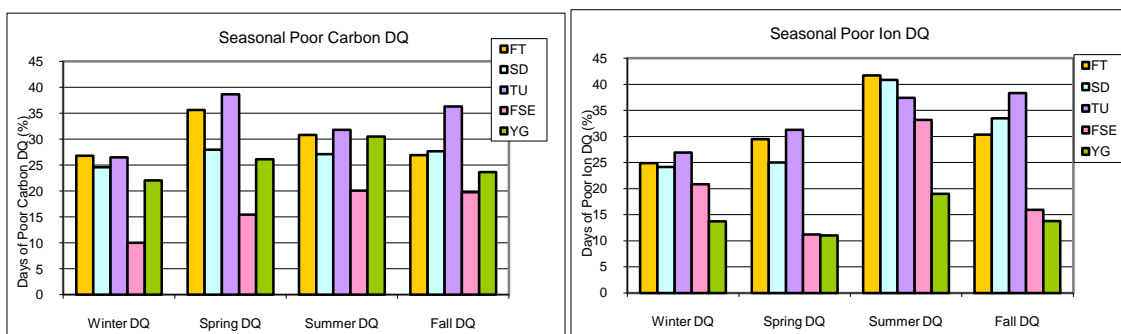


Figure 19- Average seasonal percentage of poor carbon and ion quality days

## CHAPTER 5: ION SENSITIVITY ANALYSIS

Secondary aerosols share a complex relationship with their related primary pollutants and efforts are continually being made to understand this dynamic relationship. ISORROPIA is a computational model which uses thermodynamic equilibrium principles to predict the relationships between common gas phase pollutants and associated aerosols. Sensitivity analyses were performed in ISORROPIA using the ASACA data set as well as SEARCH data from the Jefferson St. site (JST) to understand the temporal and spatial variation in the limiting components of secondary inorganic aerosol formation in the Atlanta region. This study focuses on sulfate, nitrate, and ammonium aerosols. Sulfate exists in aerosols as sulfuric acid ( $\text{H}_2\text{SO}_4$ ), ammonium bisulfate ( $\text{NH}_4\text{HSO}_4$ ), and ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) and some mixed  $\text{NH}_4\text{-SO}_4\text{-NO}_3$ . The relative amounts of each of these species are dependent on the amount of  $\text{NH}_4^+$  available for neutralization. Nitrate aerosol primarily exists as ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and is therefore also highly dependent on the  $\text{NH}_4^+$  available. Due to the volatility of ammonium nitrate, the ambient temperature and relative humidity also play an important role in its formation.

The first analysis estimates the sensitivity of the total ambient concentration of a species (gas + aerosol) to a perturbation in the aerosol phase of that particular species. Figure 20 shows the flow of sulfate, nitrate and ammonium through a reverse analysis in ISORROPIA and the resulting total concentrations. The resulting sensitivity is calculated as the difference in the total concentrations of a species predicted by the perturbed aerosol case and the base aerosol case divided by the magnitude of the induced change in

aerosol concentration as shown in the equations below. In this study the change in concentration used for all species is  $0.1 \mu\text{g}/\text{m}^3$ . Also,  $\text{NH}_3$  concentration is set to not exceed  $2 \mu\text{g}/\text{m}^3$ . This limit is set due to frequent occurrences of unnaturally high concentrations of  $\text{NH}_3$  predicted by ISORROPIA. The high predicted concentrations could result from a lack of temporal resolution because 24 hr average relative humidity and temperature are used.

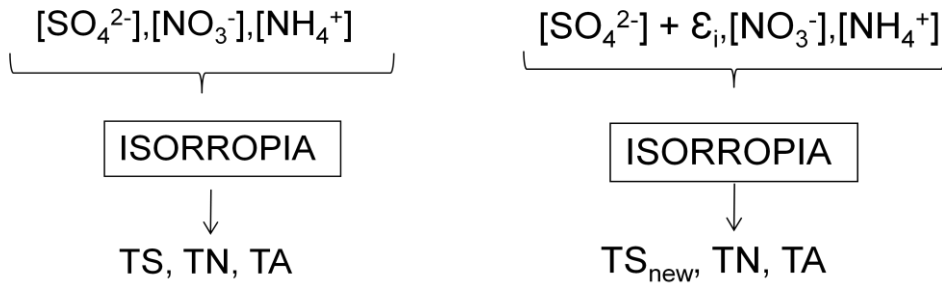


Figure 20 Flow of data for the total sulfate (TS) sensitivity to sulfate aerosol

$$S_{ij} = \frac{[T_i(B + \varepsilon_i)] - [T_i(B)]}{\varepsilon_i} \quad ; \quad i - \text{species perturbed}$$

The seasonal averaged sensitivity results from the analysis of 1999 to 2008 ASACA data are summarized in Figure 21 and 22. The sensitivity of total nitrate to nitrate aerosol tends to fluctuate from 1 to 3, while the sulfate sensitivity rarely deviates from 1. Under ambient conditions, virtually no sulfuric acid exists in a gaseous form. Therefore an addition of  $0.1 \mu\text{g}/\text{m}^3$  of sulfate aerosol will increase the total amount of aerosol by  $0.1 \mu\text{g}/\text{m}^3$ . The magnitude of the seasonal variation in total nitrate sensitivity increased from 1999 until 2003 when the peaks decreased. Seasonal sensitivity variations proceed to increase after 2005 for the ASACA sites, while the sensitivity at JST remains fairly constant. The peak sensitivities tend to occur during summer months



and dips occur during winter months. The maximum nitrate sensitivity of 2.94 occurs at FT during the summer of 2008, meaning that it would take an increase of  $2 \mu\text{g}/\text{m}^3$  of nitrate gas to increase the nitrate aerosol concentration by  $1 \mu\text{g}/\text{m}^3$ .

The ammonia sensitivity trend is less definite than the nitrate sensitivity; however peaks frequently occur in fall and spring months. Also, the minimum ammonium sensitivity is 1.3 during the summer of 2002 and the sensitivity for JST rarely dips below 1.5, indicating that there are rarely cases in which all of the ammonium is in aerosol form. In other words, in order to increase the aerosol concentration of ammonium by a certain value, ammonia would have to increase by an even greater value for any given season.

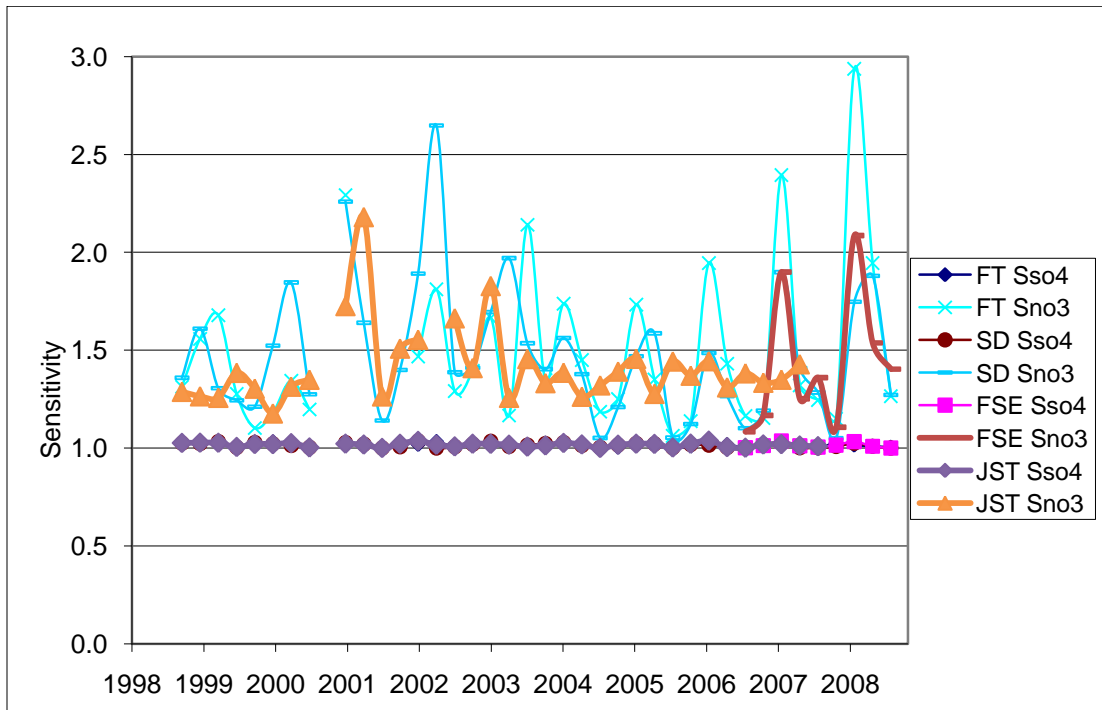


Figure 21- Seasonal average sensitivity of total sulfate and nitrate to aerosol sulfate and nitrate (1999-2008). Sso4 and Sno3 are the sensitivities of total sulfate and nitrate gas to their aerosol phases.

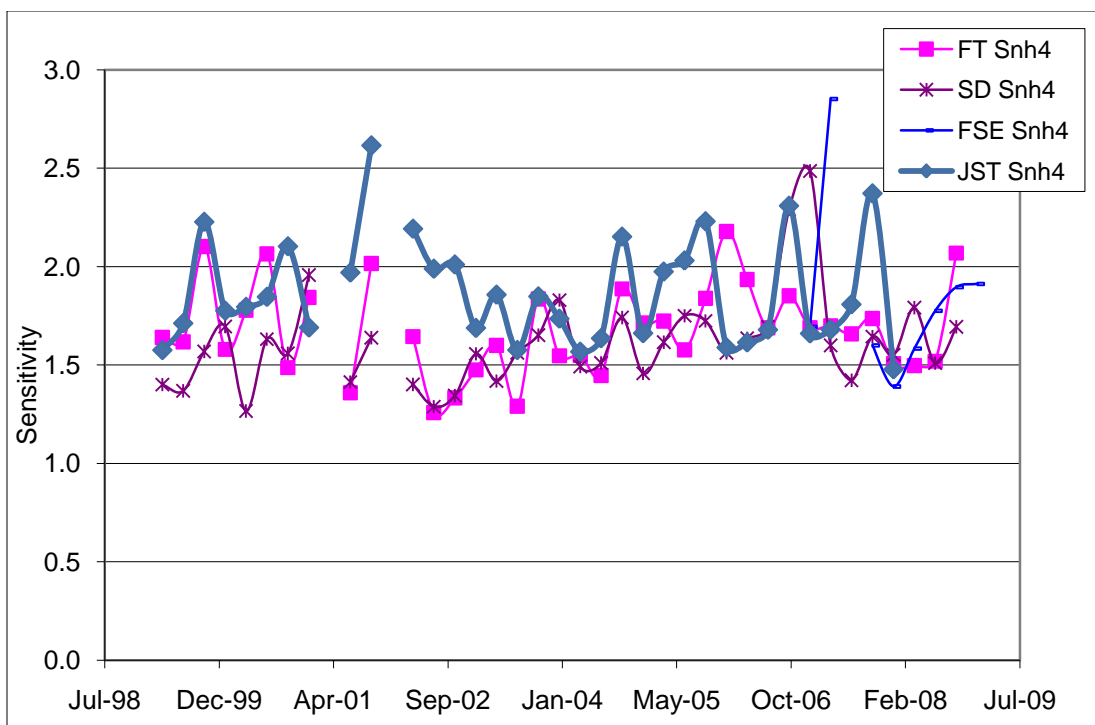


Figure 22- Seasonal average of total ammonia sensitivity to ammonia aerosol (1999-2008)

The seasonal effects on the aerosol-gas phase dynamics are apparent when comparing the average seasonal sensitivities (ASACA site average) (Figure 23). The nitrate sensitivity peaks and exceeds ammonia sensitivity only during the summer months. As explained before, the volatility of ammonium nitrate limits the amount of nitrate aerosol. Also, during the summer, sulfate is high in concentration due to increased photochemical activity and is readily available to bind most if not virtually all of the ammonia needed to form ammonium nitrate. Ammonia sensitivities, on the other hand, peak in the fall and reach a minimum during the winter. The high sensitivity in the fall is most likely due to a combination of increased volatility from relatively high temperatures and decreased amount of available sulfate aerosol from summer months.

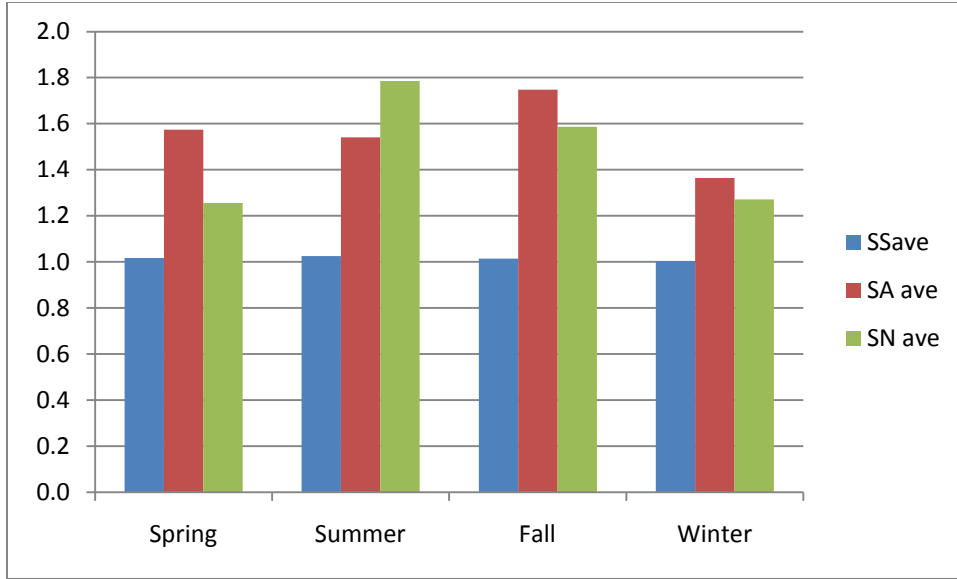


Figure 23- Seasonal average sensitivities of total sulfate (SS), nitrate (SN) and ammonia (SA) to their respective aerosol phase (average of all ASACA sites)

The second sensitivity analysis predicts the sensitivity of total  $PM_{2.5}$  mass to a change in the total concentration of a species. For this study, total  $PM_{2.5}$  mass refers to secondary inorganic aerosol mass (organic and elemental carbon are not included). Total sulfate, nitrate and ammonia concentrations predicted by a reverse run in ISORROPIA are increased slightly and new  $PM_{2.5}$  concentrations are predicted in a forward run of ISORROPIA (Figure 24). The sensitivities are then calculated as:

$$S_{PM_{2.5},i} = \frac{[PM_{2.5}(B + \varepsilon_i)] - [PM_{2.5}(B)]}{\varepsilon_i} \quad i - \text{species perturbed}$$

$$GR = \frac{\{TA\} - 2\{TS\}}{\{TN\}}$$

The species with the greatest sensitivity at any given period is defined as the limiting species. The gas ratio (GR) is also used to quantify the availability of ammonia as a neutralizer. It takes into account the ambient molarities of the total sulfate and nitrate and to what extent the ammonia can neutralize the atmospheric sulfuric and nitric acid. Table 10 summarizes the implications of various GR values.

Table 10- Description of Gas Ratio values

GR	Description
<0	insufficient ammonia to neutralize all of the sulfate
>0 and <1	enough ammonia to neutralize sulfate but not nitrate
>1	sufficient ammonia to neutralize sulfate and at least part of the nitric acid

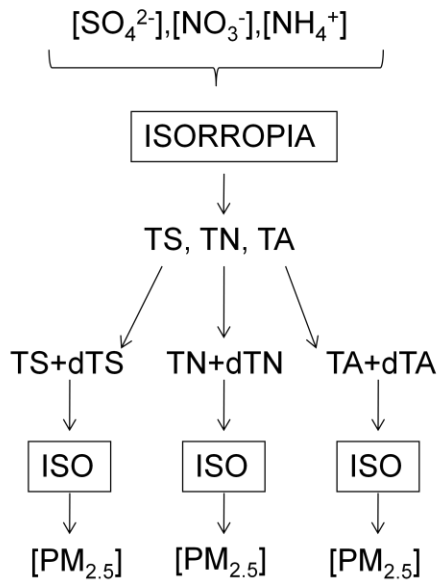


Figure 24- Flow of data for the PM sensitivity to total species concentration

The sensitivity due to nitrate and the gas ratio consistently peak and dip during the same periods, while sensitivity due to ammonia is anti-correlated to these (Figure 25 and 26). Peaks in sensitivity due to ammonia range from 1.0 to 1.6 while nitrate peaks stay below 1.24. The maximum theoretical  $\text{PM}_{2.5}$  sensitivity to nitrate occurs in the case that all of the nitrate added is neutralized by ammonia gas and converted to aerosol as ammonium nitrate. This case corresponds to a sensitivity of 1.29. The upper bound of sulfate sensitivity can be calculated in a similar way and is 1.38. The sulfate sensitivity also follows a similar trend as the gas ratio, though the magnitude of the peaks and dips is less than that of the nitrate sensitivity. The difference is due to the necessity of ammonia for nitrate to form aerosol while sulfate will be in the aerosol form regardless.

From winter 2004 to fall 2007, a period characterized in the previous chapter by high data quality, the peaks in the GR and nitrate occur primarily during winter months. Ammonia sensitivity during that time period is inversely correlated to nitrate sensitivity and the GR. The remainder of the years tested experience more sporadic peaks and dips indicating that the reliability of data plays an important role in sensitivity analysis performance.

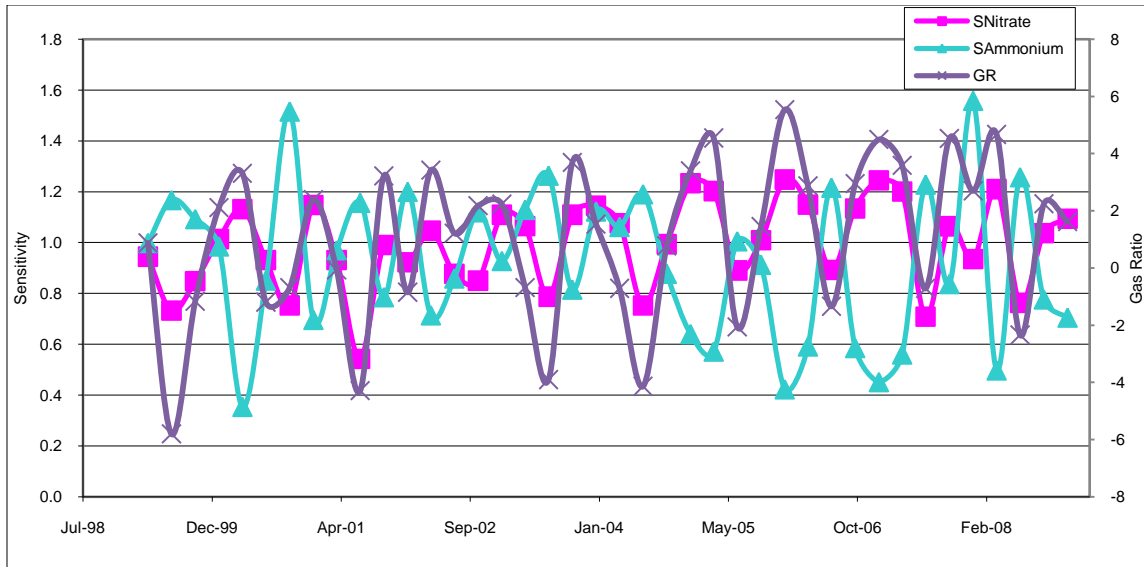


Figure 25- Seasonal average  $PM_{2.5}$  sensitivities to nitrate and ammonia. Seasonal average gas ratios (1999-2008)

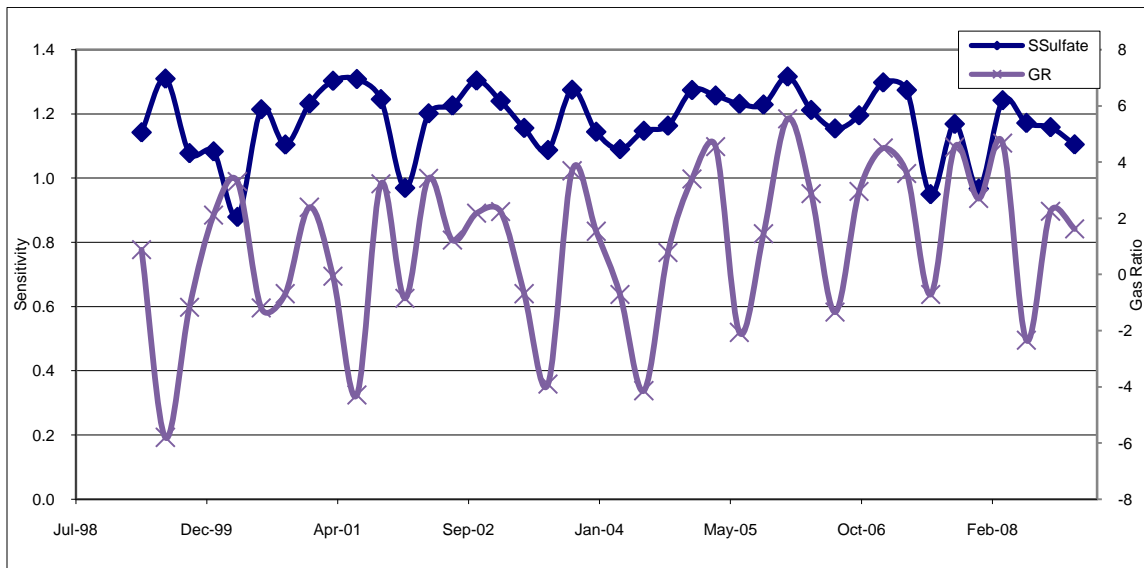


Figure 26- Seasonal average  $PM_{2.5}$  sensitivity to sulfate and seasonal gas ratios (1999-2008)

The seasonal  $PM_{2.5}$  sensitivities to its various components are averaged from 1999 to 2008 for clarity of seasonal variations (Figure 27). The average gas ratios as well as total number of days that sensitivity of  $PM_{2.5}$  to sulfate is negative (NN) are included in

Table 11. Average sulfate sensitivity peaks in the fall at 1.2 and is at a minimum during the winter. The sensitivity due to sulfate is consistently greater than the sensitivities due to nitrate and ammonium indicating the importance of sulfate in aerosol formation year round. On some days however, an increase in sulfate causes the total  $PM_{2.5}$  mass to decrease. The addition of one molecule of sulfate can take two molecules of ammonium from ammonium nitrate, displacing two molecules of nitrate; thus the aerosol mass decreases. A theoretical minimum sensitivity in this case is -0.29. This phenomenon occurred 33 times during winter months and only 19 times during summer months according to this sensitivity analysis. Ammonium nitrate is more abundant during winter months while ammonia gas concentration is relatively low.

$PM_{2.5}$  sensitivities to nitrate and ammonium appear to be more greatly influenced by the seasons. Sensitivity to ammonia peaks in the summer at 1.12, while sensitivity to nitrate reaches a minimum of 0.79 at the same. These results imply that summer time aerosol is more limited by ammonia than nitrate. As mentioned earlier, the volatility of ammonium nitrate limits its ability to form in an aerosol during summer months when temperatures are high. At the same time, increased photochemical activity produces an abundance of available sulfate for ammonia to neutralize, as indicated by the negative gas ratio.

During the remaining seasons, nitrate has a greater impact on aerosol mass than ammonia, especially in the winter and spring. Sensitivity to nitrate peaks in the winter at 1.1 and decreases only slightly during the spring. Sensitivity to ammonia reaches a minimum of 0.74 during the spring. The greatest difference in sensitivities occurs during the spring. The gas ratio values during winter and spring are 2.8 and 2.5, indicating that

there is enough ammonia present to neutralize all of the sulfate and nitrate. Also, low temperatures and high relative humidity during the winter provide optimal conditions for ammonium nitrate to form while sulfate concentrations are relatively low.

Table 11- Average ASACA seasonal gas ratios and number of negative PM<sub>2.5</sub> sensitivities to sulfate

	GR	NN
<b>Spring</b>	2.18	30
<b>Summer</b>	-2.46	19
<b>Fall</b>	1.92	23
<b>Winter</b>	2.52	33

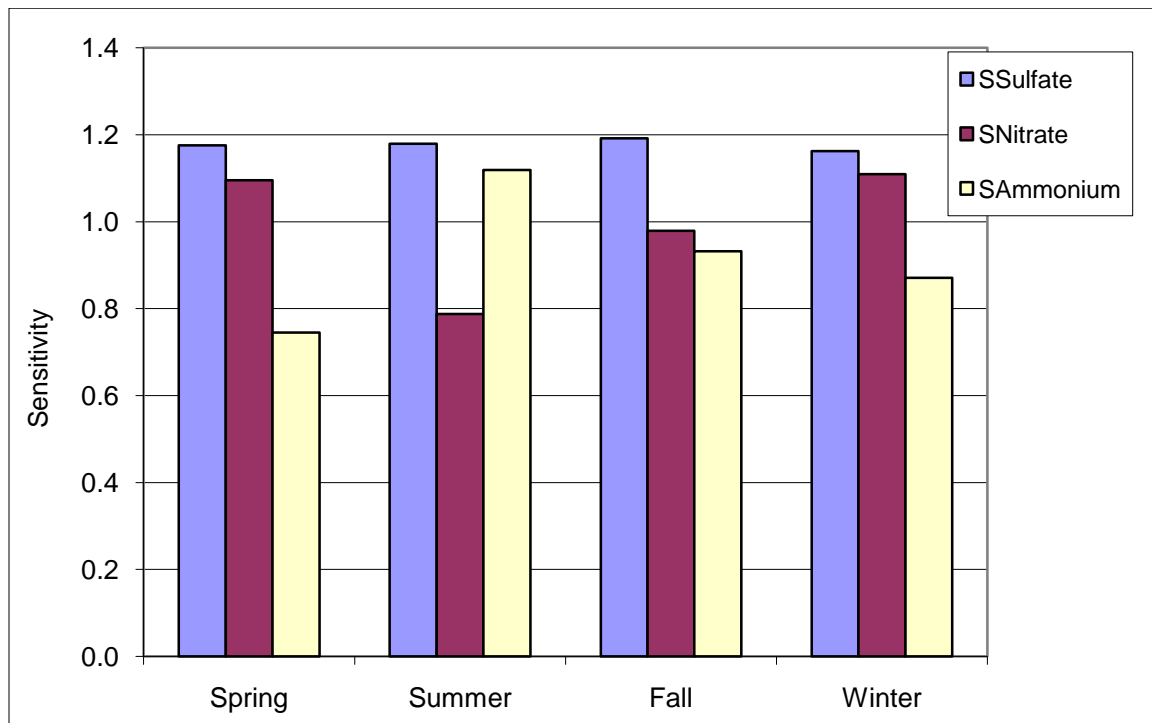


Figure 27- Average seasonal PM<sub>2.5</sub> sensitivity to sulfate, nitrate and ammonia (1999-2008).



## CHAPTER 6: CONCLUSION

ASACA PM<sub>2.5</sub> from 1999 to 2008 has been collected and analyzed to understand spatial and temporal variations in ambient concentrations of ionic, carbonaceous, and metallic aerosol species. The data suggest that total PM<sub>2.5</sub> mass has decreased slightly in the past ten years while its composition has remained constant and its spatial variability continues to be fairly homogeneous. PM concentration tends to be highest during the summer and decreases during the winter primarily due to changes in photochemical activity. All secondary aerosol species ambient concentrations, with the exception of nitrate, peak in the summer, indicating high photochemical activity. Nitrate concentrations peak in the winter when temperatures are low and ammonia is available to neutralize nitric acid.

ASACA data quality values increased from around 5 at its inception in 1999 to around 9 in 2004. Before 2004, poor data quality is attributed mainly to missing PM component data. Mass closure results and comparisons with non-ASACA sites indicate that, when all components of PM<sub>2.5</sub> are available, the data before 2004 are valid. From 2005 to 2008, yearly averages of the data quality from each analytical metric support the validity of ASACA data and methodology during that time. Seasonal variations in various components of ASACA data quality are also apparent throughout the collection period. Poor data quality during the summer, particularly in the ionic species data, can probably be attributed to volatility of secondary components of PM<sub>2.5</sub>. This source of error is difficult to control but can be minimized by following filter handling and storage procedures.

Temporal characteristics of the thermodynamic relationship between major secondary aerosol components and their associated precursor gases were described by using ASACA PM<sub>2.5</sub> data as an input to ISORROPIA. The first sensitivity analysis suggests that it would take a massive change in nitrates precursor gases to affect nitrate aerosol during the summer due to the lack of available ammonia. However, during the winter, nitrate aerosol is more directly affected by a change in its precursor gases.

The results of the second sensitivity analysis support the idea that aerosol formation is highly limited by sulfate concentrations all year long, with the exception being the days when sulfate has a negative effect on PM<sub>2.5</sub> mass. Aerosol formation is more limited by ammonia than nitrate during the summer and vice-versa during the winter. These results not only help validate the usefulness of a clean ASACA data set, but can also be helpful when designing PM<sub>2.5</sub> control strategies and implementation plans.

## RESOURCES

- Ansari, A. S. and S. N. Pandis (1998). "Response of inorganic PM to precursor concentrations." Environmental Science & Technology 32(18): 2706-2714.
- Bergin, M. H., R. Greenwald, et al. (2001). "Influence of aerosol dry deposition on photosynthetically active radiation available to plants: A case study in the Yangtze delta region of China." Geophysical Research Letters 28(18): 3605-3608.
- Blanchard, C. L. and G. M. Hidy (2003). "Effects of changes in sulfate, ammonia, and nitric acid on particulate nitrate concentrations in the southeastern United States." Journal of the Air & Waste Management Association 53(3): 283-290.
- Butler, A. J. (2000). Temporal and Spatial Analysis of PM<sub>2.5</sub> and Composition in Atlanta. Atlanta, GA, Georgia Institute of Technology. Ph.D.
- Cary, B. (1998). Thermal/Optical Carbon Analyzer, A Guide to Running and Maintaining the Analyzer, Version 4.0. Tigard, OR, Sunset Laboratory, Inc.
- Charlson, R. J. (1969). "ATMOSPHERIC VISIBILITY RELATED TO AEROSOL MASS CONCENTRATION - A REVIEW." Environmental Science & Technology 3(10): 913-&.
- Cobb, E. (2006). Spatial and Temporal Variations of PM<sub>2.5</sub> Mass and composition in Atlanta: ASACA 1999 – 2006. Atlanta, GA, Georgia Institute of Technology. M.S.
- Dockery, D. W. (2001). "Epidemiologic evidence of cardiovascular effects of particulate air pollution." Environmental Health Perspectives 109: 483-486.
- Dockery, D. W., C. A. Pope, et al. (1993). "AN ASSOCIATION BETWEEN AIR-POLLUTION AND MORTALITY IN 6 UNITED-STATES CITIES." New England Journal of Medicine 329(24): 1753-1759.
- EPA. (2000). "PM Supersites Program Background." from <http://www.epa.gov/ttn/amtic>. Accessed: January 2010
- Habibi, K. (1973). "CHARACTERIZATION OF PARTICULATE MATTER IN VEHICLE EXHAUST." Environmental Science & Technology 7(3): 223-234.
- Hansen, A. D. A. (1999.10). The Aethalometer. Berkeley, CA, Magee Scientific Company.
- Hartsell, B. and E. Edgerton (1998). ""ARA Measurements" presented at the initial meeting for the Atlanta epidemiological study, Atlanta, GA."

- Lim, H. J. and B. J. Turpin (2002). "Origins of primary and secondary organic aerosol in Atlanta: Results of time-resolved measurements during the Atlanta supersite experiment." Environmental Science & Technology 36(21): 4489-4496.
- Lowenthal, D. H., B. Zielinska, et al. (1994). "CHARACTERIZATION OF HEAVY-DUTY DIESEL VEHICLE EMISSIONS." Atmospheric Environment 28(4): 731-743.
- Mauderly, J. L. (2001). "Diesel emissions: Is more health research still needed?" Toxicological Sciences 62(1): 6-9.
- Morgan, W. K. C., R. B. Reger, et al. (1997). "Health effects of diesel emissions." Annals of Occupational Hygiene 41(6): 643-658.
- Nenes, A., S. N. Pandis, et al. (1999). "Continued development and testing of a new thermodynamic aerosol module for urban and regional air quality models." Atmospheric Environment 33(10): 1553-1560.
- Reed, M. D., A. P. Gigliotti, et al. (2004). "Health effects of subchronic exposure to environmental levels of diesel exhaust." Inhalation Toxicology 16(4): 177-193.
- Rosenkranz, H. S. (1996). "Mutagenic nitroarenes, diesel emissions, particulate-induced mutations and cancer: An essay on cancer-causation by a moving target." Mutation Research-Genetic Toxicology 367(2): 65-72.
- Schauer, J. J., W. F. Rogge, et al. (1996). "Source apportionment of airborne particulate matter using organic compounds as tracers." Atmospheric Environment 30(22): 3837-3855.
- Sioutas, C., S. N. Pandis, et al. (2004). "Special issue of Atmospheric Environment on findings from EPA's Particulate Matter Supersites Program - Preface." Atmospheric Environment 38(20): 3101-3106.
- Takahama, S., A. E. Wittig, et al. (2004). "Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study." Journal of Geophysical Research-Atmospheres 109(D16): 10.
- Turpin, B. J. and H. J. Lim (2001). "Species contributions to PM<sub>2.5</sub> mass concentrations: Revisiting common assumptions for estimating organic mass." Aerosol Science and Technology 35(1): 602-610.
- USEPA (1997). National Ambient Air Quality Standards for Particulate Matter - Final Rule. 40 CFR part 50. U. S. E. P. Agency. 138.
- Uttell, M. J., M. W. Frampton, et al. (2002). "Cardiovascular effects associated with air pollution: Potential mechanisms and methods of testing." Inhalation Toxicology 14(12): 1231-1247.

- Wark, K., C. F. Warner, et al. (1998). Air Pollution: It's Origin and Control - 3rd ed. Menlo Park, CA, Addison Wesley Longman, Inc.
- Watson, J. G., L. W. A. Chen, et al. (2008). "Source apportionment: Findings from the US Supersites program." Journal of the Air & Waste Management Association 58(2): 265-288.
- West, J. J., A. S. Ansari, et al. (1999). "Marginal PM<sub>2.5</sub>: Nonlinear aerosol mass response to sulfate reductions in the Eastern United States." Journal of the Air & Waste Management Association 49(12): 1415-1424.
- Wexler, A. S. and M. V. Johnston (2008). "What have we learned from highly time-resolved measurements during EPA's Supersites program, and related studies?" Journal of the Air & Waste Management Association 58(2): 303-319.